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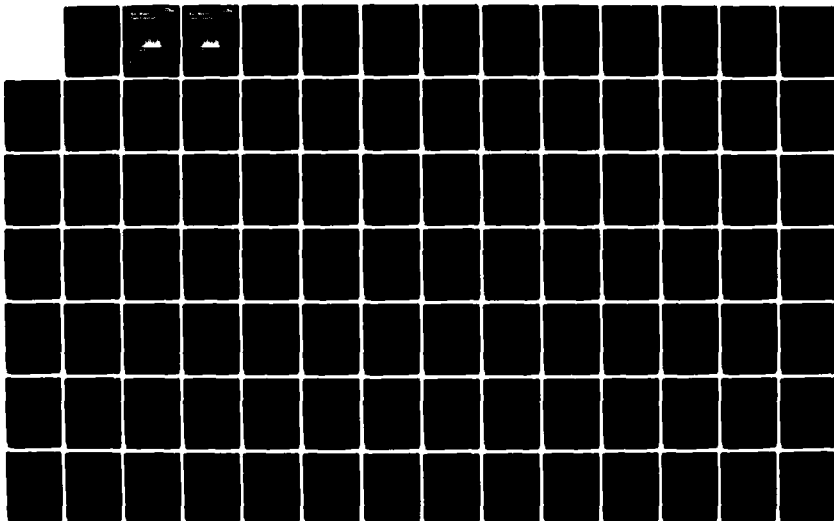
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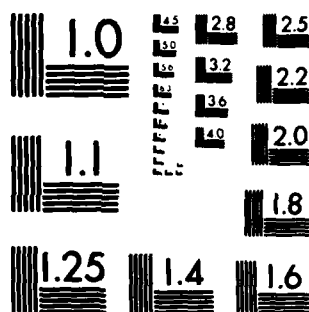
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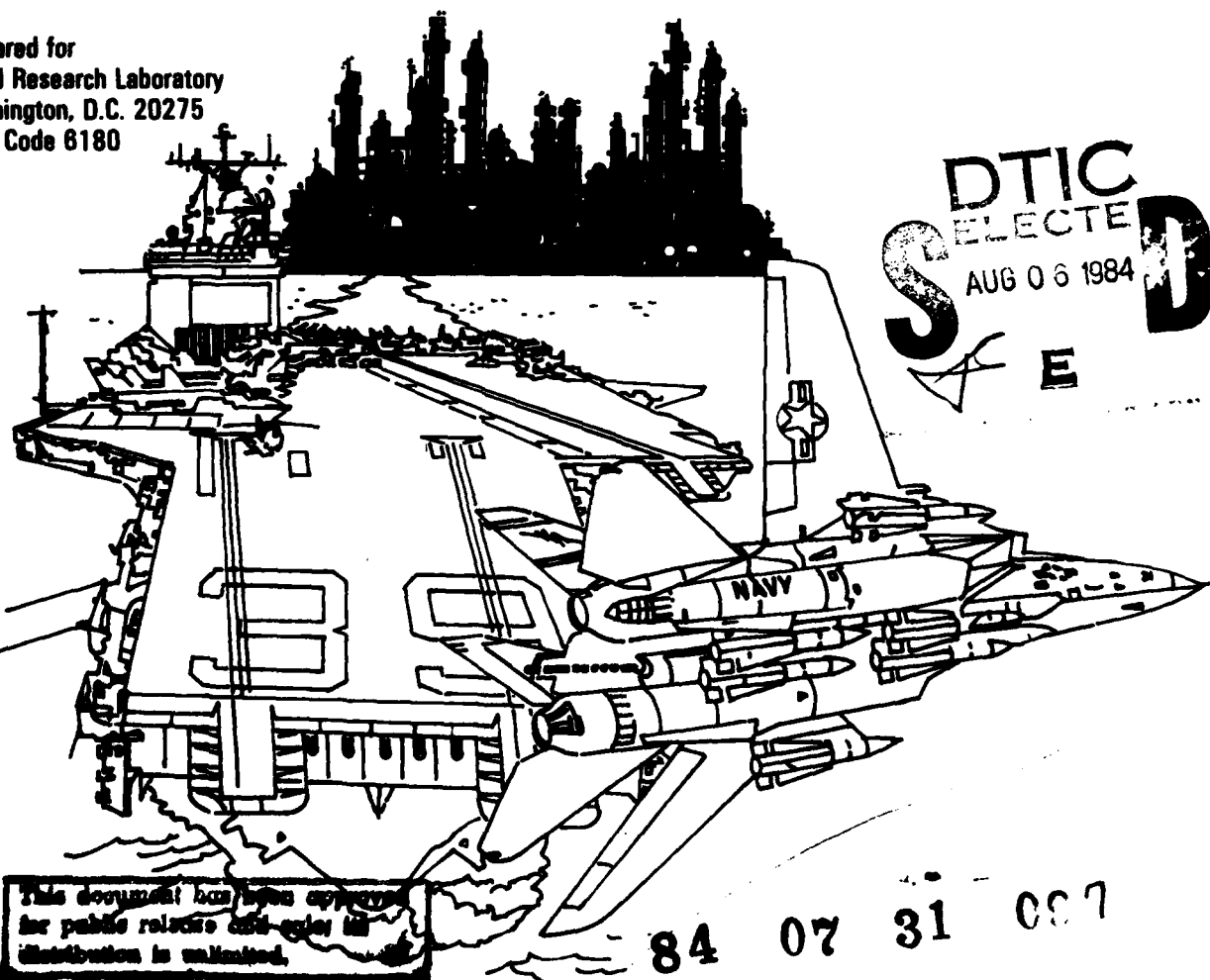
Final Report
July 20, 1984

Contract No.
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Prepared by
Chemistry Laboratory
TRW Energy Development
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One Space Park,
Redondo Beach, CA 90278

Prepared for
Naval Research Laboratory
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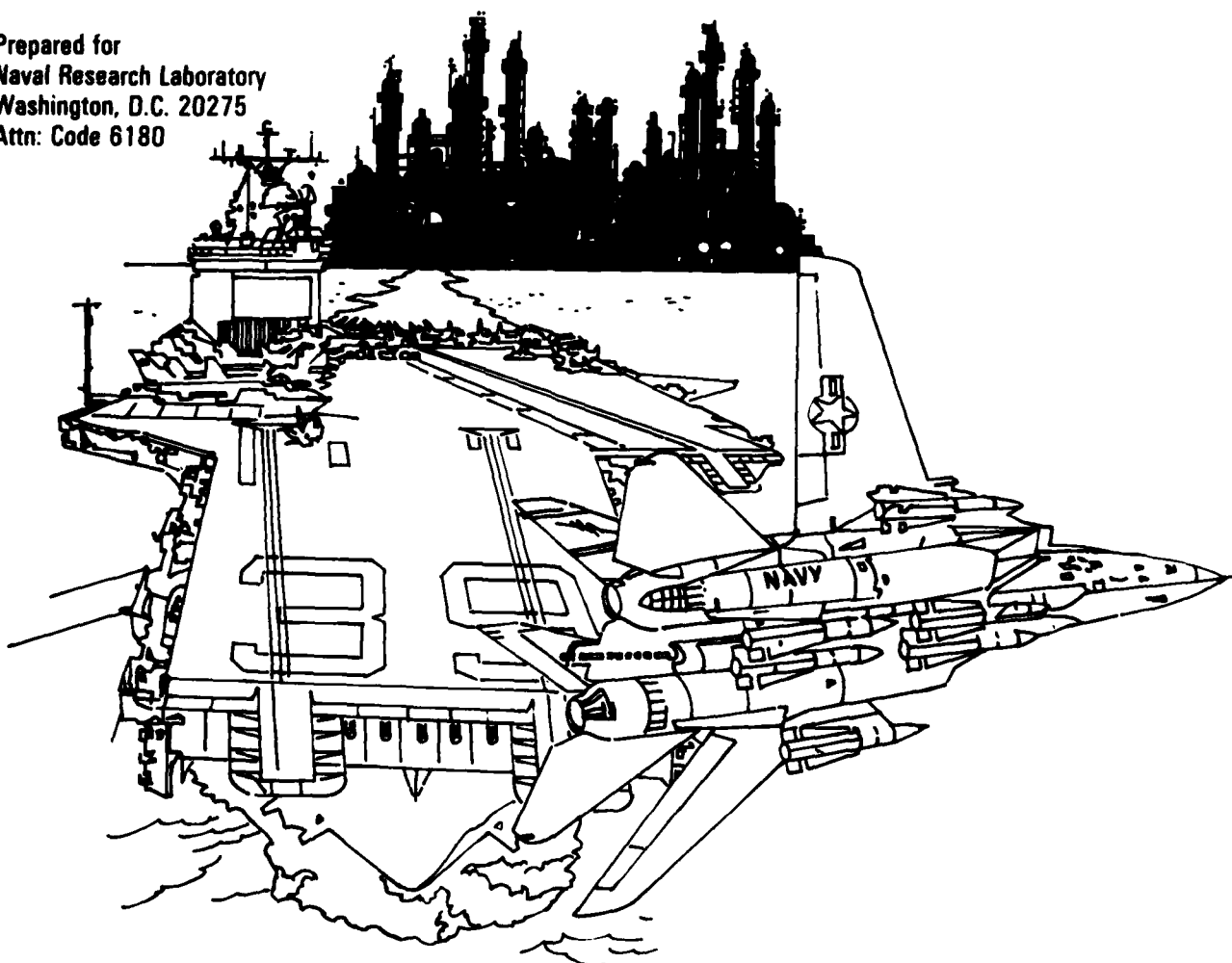
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qualified. For the resolution of the lubricity testing problem, it has been demonstrated that the TRW/Lucas Tester provides reproducible values of the friction factor, a property of the fuel itself, which relates directly to boundary lubrication and gear scoring. Friction factor measurements of all nine qualified corrosion inhibitors in clay-filtered isooctane revealed that lubricity reaches a maximum value at about 2 ppm and remains unchanged with further increases in additive concentration. HITEC E-515 was shown to provide very rapid decreases in friction factor at such ppm levels, as did all other products with slightly superior performance on the part of LUBRIZOL 541 and slightly weaker by UNICOR-2. This demonstration of reliable lubricity evaluation is considered a major break-through.

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FORWARD AND ACKNOWLEDGEMENTS

This is the final report of an 18 month program performed by TRW's Chemistry Laboratory, managed by Dr. E. D. Guth. The Chemistry Laboratory is a part of the Energy Technology Division, under TRW's Energy Development Group.

Dr. Erwin Fishman was the program manager. The very able technical crew consisted of Dr. Martin Mach, Analytical Chemistry, Ms. Leslye Fraser, Material Compatibility, and Mr. David Moore, Lubricity. Important technical guidance was provided by Mr. Jon Martin in the area of elastomer compounding and testing.

A special in-house acknowledgement is reserved for Mr. Carl Nau and David Laws of TRW's Power Accessories Division in Cleveland, Ohio. Mr. Nau modified the Lucas Dwell Tester to change it from an instrument counting "dwell number" to a precision device for measurement of the friction factor, a lubricity related property of the fuel itself. Under his supervision, Mr. Laws performed most of the friction factor tests reported here. To this team is due much credit for providing a sound technical foundation for the field of fuel lubricity.

It is a special pleasure to acknowledge interest and involvement on the government side. First to Dr. Robert N. Hazlett of the Naval Research Laboratory, who, as technical monitor of this program, read all the quarterly reports with care and understanding and offered guidance from the considerable reservoir of his experience as a fuels chemist. He was a model major monitor. Mr. Buck Nowack of the Naval Air Propulsion Center funded this program out of his hard-won R&D funds. He was expertly assisted by Mr. Rick Kamen and Mr. Peter Karpovich who made important contributions to the lubricity task. Finally, we must thank Dr. Theodore A. Jacobs, Assistant Secretary of the Navy, Research, Applied and Space Technology, whose confidence in our ability to make original contributions to fuel technology lead to this program.

ABSTRACT

There were three tasks in this program: 1) Analytical Chemistry of sulfur species in JP-5; 2) Materials Compatibility; 3) Lubricity. In task 1 it was found that pre-separation steps were essential prior to compound identification. Various forms of HPLC were inadequate pre-separation methods. A chromatographic process coupled with oxidation and reduction of eluate, developed by Prof. Milton Lee, was successful in providing samples from which a group of aromatic thiophenes were identified by GC/MS. Aromatic thiophenes were found to constitute 90% of the sulfur content of JP-5's, with sulfides, disulfides and mercaptans at the ppm level. Further refinements of the Lee Method are required to improve sulfur mass closure. The Materials Compatibility task accomplished quantitative measurements of the degradation of Milspec nitrile rubber, widely used for fuel system seals, in the presence of peroxide formed in JP-5. The vulnerability of nitrile rubber to fuel peroxide was shown to be determined by backbone unsaturation. The stability of nitrile rubbers was shown to be independent of the concentration of four different aromatics. Alternate elastomers insensitive to fuel peroxide were tested, including AFLAS/EPDM terblend, PNF-280-009 and Zetpol, but further development is needed before these are fully qualified. For the resolution of the lubricity testing problem, it has been demonstrated that the TRW/Lucas Tester provides reproducible values of the friction factor, a property of the fuel itself, which relates directly to boundary lubrication and gear scoring. Friction factor measurements of all nine qualified corrosion inhibitors in clay-filtered isooctane revealed that lubricity reaches a maximum value at about 2 ppm and remains unchanged with further increases in additive concentration. HITEC E-515 was shown to provide very rapid decreases in friction factor at such ppm levels, as did all other products with slightly superior performance on the part of LUBRIZOL 541 and slightly weaker by UNICOR-2. This demonstration of reliable lubricity evaluation is considered a major break-through.

1.0 INTRODUCTION AND SUMMARY

In response to the ever increasing production of mobility fuels from high sulfur and high gravity crudes, the Navy has placed a priority on understanding the interactions of fuel composition, physical properties, and fuel system performance. The Navy has stated that one of its objectives in the current Aircraft/Mobility Fuels Program is to "Assess the impact on performance of Navy systems of relaxing current military fuel specifications." Such an assessment requires an expansion of the data base on the impact of specific fuel components on the behavior of fuel-related hardware.

TRW has structured its Navy Mobility Fuels program to investigate fuel-hardware impacts in two areas: fuel lubricity and fuel elastomer compatibility. Another component of the program is the advancement of the state-of-the-art of the analytical chemistry of sulfur compounds contained in distillate fuels. Further analytical chemistry advances are contemplated for this program in order to enhance the prospects of finding direct causal relations between fuel composition and fuel/hardware behavior.

It is intended that testing and analytical developments be performed on JP-5 fuel as procured by the Navy except for the use of analogues where required for control of composition. When received, fuel samples are normally placed in refrigeration, under nitrogen in glass containers. Samples as received are given a NFP-X number. The samples used in this program are listed and described in Appendix A.

1.1 ORGANIZATION OF THIS REPORT

The report begins with summaries of the accomplishments in each of the three tasks: Analytical Chemistry, Material Compatibility and Lubricity. These summaries are intended to inform those readers who want to survey the program without digging into detailed experimental descriptions and results.

After the summaries, the report continues with three sections, self contained, giving full descriptions of the experiments carried out. Details which are felt to interrupt the flow of the text are placed in the Appendix. Not all approaches taken in this program produced the desired results, but all

are included with the intention of aiding future jet fuel researchers to steer a productive course.

1.2 SUMMARY OF ANALYTICAL CHEMISTRY TASK

The Analytical Chemistry Task was dedicated to finding methods for determining the concentration of each sulfur-containing species present in a sample of JP-5. That this is a formidable task can be seen by noting that the total sulfur content of JP-5 is generally less than 0.5%, that this sulfur content is made up of possibly thousands of species which are distinct chemical entities, and that these objects of our search are buried in a matrix of hundreds of thousands of mainly hydrocarbon species having physical and chemical properties similar to their sulfur bearing counterparts.

The approach taken was to perform a series of separations, physical and chemical, designed to isolate the sulfur compounds from the rest and the different classes of sulfur compounds from each other. This separation is then followed by analysis designed to provide specific compound identification by mass spectrometry when previous separations will permit spectral identification by removing domineering interferences. This is rather like identifying individual criminals in a large population by first separating all the law-abiding citizens and then interviewing those who remain.

The approach has three main constituents:

- 1) Separation of sulfur compounds, present at levels of 0.1-0.5% (as sulfur), from the bulk of hydrocarbons.
- 2) Qualitative analysis of the separated sulfur compounds to identify them by class (e.g., benzothiophene, mercaptan), boiling point range, or as individual compounds, and
- 3) Quantitative analysis of sulfur in the separated fractions as compared to the as-received fuel to check for sulfur mass balance.

Our initial studies attempted to identify sulfur compounds in JP-5 directly, i.e., without some prior separation from the hydrocarbons, using capillary gas chromatography (GC) with the column effluent split to a flame

ionization detector (FID) to detect all carbon-containing compounds and a Hall electrolytic conductivity detector in the sulfur mode (HECD-S) for specific detection of sulfur compounds. This simple approach was quickly abandoned. The HECD-S could usually detect sulfur compounds that co-eluted with hydrocarbons, but these compounds could not be identified by GC-Mass spectrometry (GC-MS) because their mass spectra were overwhelmed by the high concentrations of hydrocarbon ion fragments.

In the first approach to overcoming this difficulty, the fuel was separated into aliphatic, and 1-, 2-, and 3- ring aromatic fractions by high performance liquid chromatography (HPLC) on normal phase silica gel, followed by GC-FID/HECD-S analysis of the individual fractions. While this resulted in separating the sulfur compounds from the aliphatic hydrocarbons, which comprise 80% of the JP-5 fuel, we were still not able to isolate the sulfur compounds from the remaining alkylbenzenes, naphthalenes, and anthracenes sufficiently to allow their identification by GC/MS.

To achieve a more detailed picture of the sulfur compound distribution, the classes of sulfur compounds present (e.g., mercaptans, benzothiophenes, sulfides) were determined by a qualitative analysis scheme developed by Ball at the U. S. Bureau of Mines. In this method, different sulfur classes are sequentially removed in a series of reactions and the amounts of each class determined by difference. It should be stressed that the chemical separation methods were attempted only with some trepidation, because of the possibility of artifacts and sample losses that might cloud the true picture of sulfur compound distribution. The chemical methods were performed only after further attempts to isolate the sulfur compounds by improved HPLC methods were unsuccessful.

Each chemically treated sample was fractionated by HPLC to further simplify the sulfur analysis, and individual fractions analyzed by capillary GC for changes in the sulfur chromatogram compared to HPLC-fractionated as-received fuel. The GC data showed very little change in the pattern of sulfur compounds, which, according to the reaction scheme, meant that most of the sulfur compounds present are benzothiophenes (BT) or dibenzothiophenes (DBT). Additional chemical assays on as-received fuel showed only low ppm

amounts of mercaptans and disulfides, indirect corroboration that the principal class of sulfur compounds in JP-5 are, in fact, BTs.

Once it was established that the BTs were the principal class of sulfur compounds in JP-5, these compounds were separated from the hydrocarbons by a method developed by M. L. Lee at Brigham Young University, based on a series of oxidations and reductions, with intermediate liquid chromatography separations. A flow diagram of this method is shown and described in detail in Section 2.3. The isolated polycyclic aromatic sulfur heterocycle (PASH) fraction from JP-5 fuel, designated NFP-1, contained the 60 individual alkyl-BTs and alkyl-DBTs as shown by GC/MS analysis. Some sulfur compounds were "lost" by irreversible oxidation, either degraded to water soluble material or eluted with an alternate fraction that may contain, for example, hydroxy-BTs.

The isolated BTs and DBT were analyzed by GC-FID/HECD-S and individual compounds catalogued by retention index (RI) according to their interpolated retention time between naphthalene (RI \equiv 2000) and phenanthrene (RI \equiv 3000). Agreement in RI between sulfur compounds in the PASH and as-received fuels was only fair, most likely because of the complexity of the mixtures and the somewhat arbitrary selection method used to choose sulfur-containing peaks in the as-received samples.

Sulfur mass balance analysis was done on the combined [PASH + HQ] fractions versus the as-received fuel to determine if any sulfur was lost during the oxidation, reduction and LC steps. Assays by x-ray fluorescence (XRF) gave poor results, with the PASH and HQ values sometimes higher (140%) and lower (43%) than the as-received fuel.

In order to see if there are any differences in the boiling point distribution of sulfur compounds between fuels, simulated distillation curves for sulfur compounds in the PASH fractions and as-received fuels were determined by capillary GC. The as-received curves for the sulfur compounds showed roughly the same boiling point distribution as the hydrocarbon components, while the PASH (BT) fraction was centered (the "50% off" point) 30-50°C higher than the hydrocarbons. While previous chemical class analysis showed that BTs were the principal sulfur component in the fuels, some as-yet unknown chemical reactions in the Lee method are most likely selectively removing lower boiling components or producing higher ones, skewing the

boiling point data to higher values. Our proposed follow-on program, in which the sulfur compounds are separated in a two-step HPLC method (silica gel/silver nitrate) should effectively eliminate these chemical artifacts and lead to a better comparison between the sulfur compounds in as-received and isolated fractions.

Finally, analysis of metals in as-received fuels by inductively coupled argon plasma spectrometry showed <1ppm concentrations of K, Mg, Pb, and V, with sub-to-low ppm amounts of Na and Ca.

1.3 SUMMARY OF THE MATERIALS COMPATIBILITY TASK

The objective of this task is to determine the vulnerability of Navy specified nitrile rubber seal compounds to hydroperoxides and aromatics in JP-5 fuel, as well as to formulate alternative elastomers which are more peroxide-resistant than the material currently specified.

A survey of contractors conducted by NAVAIR regarding elastomers used in airframe fuel systems and how their behavior indicated the Navy primarily uses a variety of nitrile rubber, which is degraded (embrittled) by peroxides in JP-5. Following a conversation with Coleman Nadler of the Naval Air Development Center, it was agreed that TRW would use a compound conforming to MIL-P-83461 as the nitrile control throughout the program. Navy sources also stated that the extreme temperature range for Navy jet fuels is -44° to 150°C (-47° to 300°F); thus, testing at TRW was conducted in this range.

Rubber formulations studied under this program, including the MIL-P-83461 control, were compounded and tested in-house, enabling TRW to retain full knowledge of rubber compositions. Testing was separated into studies with nitrile rubber and alternative polymer systems.

1.3.1 Studies with Nitrile Rubber

TRW started the program with an attempt to identify a chemical that would catalytically decompose peroxides when added either to a rubber compound or JP-5, without altering the rubber's properties. Following a search of Chemical Abstracts, two such chemicals were chosen for study: iron phthalocyanine and manganese dioxide (MnO₂). Work with the former was discontinued as its property of enhancing oxygen transport, hence the build-up

of peroxide levels, was shown in this application to dominate any tendency it has to catalyze peroxide decomposition.

Extensive testing was conducted with MnO_2 . It was evaluated both as an additive to a MIL-P-83461 nitrile compound, as well as to JP-5. However, testing showed that although MnO_2 did not interfere with the cure of the nitrile, or affect the nitrile's modulus, tensile strength, or hardness, it also did not increase the nitrile's resistance to peroxide attack.

Experiments were also conducted with nitrile:EPDM blends. Nitrile polymer contains residual unsaturation in the butadiene component of its backbone structure; EPDM is a completely saturated hydrocarbon. By varying the EPDM content of the blends, the percent unsaturation of the backbone was varied. Exposing the blends to peroxidized JP-5 showed a positive relationship between backbone polymer unsaturation and compound degradation; i.e., the Navy can improve a seal's performance by increasing the acrylonitrile content (and thus decreasing the unsaturation content) of the nitrile polymer used.

A study to determine the effects of aromatics in JP-5 on nitrile degradation was also conducted. It has been proposed that hydroperoxides form most readily on aromatic structures, and it is known that hydroperoxides cause nitriles to degrade by attacking the unsaturation points in the copolymer backbone.

Four conventional nitrile compounds based on copolymers which vary in acrylonitrile content from 27 to 50 mole-percent were evaluated, as well as one compound based on a newly-developed highly-saturated (backbone) copolymer. The aromatics added to the fuel at levels of 5% W/W and 25% W/W were mesitylene, durene, and dimethylnaphthalene. These compounds were selected as being representative of those aromatics present in JP-5 over its boiling range. Aging was conducted at 71°C (160°F) for up to eight weeks. Results of the study indicated that:

- Conventional unsaturated nitriles with an acrylonitrile content of 40 mole-% are best able to resist degradation caused by aromatics;

- The ability of conventional nitriles to withstand degradation caused by the aromatics is independent of the concentration of aromatics between 5 and 25% w/w.

Nitrile polymers may be cured with peroxides as well as with sulfur, the conventional curing agent. An experiment was conducted to determine if changing to a mixed sulfur/peroxide cure system would provide a nitrile compound which is more resistant to peroxide attack, as sulfur and peroxide attack different sites on the polymer backbone. Results from the study do not show the mixed cure system to increase nitriles' resistance to degradation caused by peroxide in JP-5.

Nippon Zeon Company, Ltd. manufactures a highly saturated nitrile (HSN) polymer produced by hydrogenating the backbone of conventional nitriles. Since these HSN polymers (Zetpol) have essentially no backbone unsaturation, they are proposed to be more stable in JP-5 containing peroxides than their conventional nitrile counterparts.

The Zetpol polymers were evaluated in a MIL-P-83461 formulation as "drop-in" substitutes for conventional saturated nitrile polymers, such as Polysar Krynac 27.50. Due to a different cure system requirement, the Zetpol polymers cannot be used as direct substitutes; however, initial studies indicate that formulations based on Zetpol polymers will offer better resistance to peroxide attack than those based on conventional polymers.

Since much of the evaluation of various compounds involved aging in JP-5 fuel, it became desirable to know the rate of peroxide growth in fuel independent of elastomeric contact. Samples of JP-5 (NFP-1) and JP-5 (NFP-2) were aged at 24°, 71°, 100°, and 135°C (75°, 160°, 212°, 275°F, respectively). Results of the study indicate that the presence of antioxidant(s) in JP-5 inhibits the growth of peroxide in the fuel. NFP-1, which contains an antioxidant(s), showed a maximum peroxide growth of 0.8 meq/l (6.5 ppm) at 100°C (212°F). In contrast, NFP-2, containing no antioxidant(s), showed a maximum growth greater than 156 meq/l (1248 ppm) at 71°C (160°F).

1.3.2 Alternative Polymer Systems

The second approach to solving the Navy's problem of degradation of nitrile seals is to specify alternative polymer systems that are more compatible with JP-5 containing peroxides.

A phosphonitrilic fluoroelastomer produced by Firestone, PNF-280-009, proved to be stable following exposure to JP-5 containing high levels of peroxide [36.5 meq/l (292 ppm)] at 135°C (275°F). However, because of relatively poor original properties, PNF-280-009 is only recommended as an alternative to static nitrile seals. Its properties are marginal for dynamic applications.

Under Air Force Contract F33615-82-C-5021, a terblend of AFLAS/EPDM/Chlorotrifluoroethylene, (hydrofluorocarbon polymer/hydrocarbon polymer/halogenated oligomer plasticizer) was developed which is stable in MIL-H-27601 fluid (a dewaxed hydrocarbon) to 316°C (600°F) and seals below -45°C (-54°F). Testing in JP-5 with 36.5 meq/l (292 ppm) peroxide at 135°C (275°F) showed the terblend was also stable under these conditions. Identified problems however were high volume swell in JP-5, and extractability of the low temperature plasticizer by the fuel. The problem of excessive swell can be counteracted by molding Aflas:EPDM seals undersized, and then swelling to size with JP-5. Aflas:EPDM blends tested after swelling with JP-5 meet both the Air Force criteria for hydraulic system seals and MIL-P-83461.

In an attempt to solve the problem of CTFE extractability by JP-5, Professor Kirby Scherer of USC was contacted to synthesize a vinyl-terminated CTFE oligomer for TRW, which could be chemically bonded into the basic polymer blend.

This material proved difficult to synthesize. Dr. Scherer provided TRW with a vinyl-terminated fluorinated plasticizer instead. The plasticizer was grafted onto the Aflas/EPDM polymer backbone (preventing extraction) before curing the compound; however, subsequent TR₁₀ tests showed the material did not lower the TR₁₀ temperature of the compound as CTFE did.

Seven other materials were also tried as alternative plasticizers:

- o Sunpar 2280 (paraffinic oil)
- o Kel-F 800 (high molecular weight CTFE)
- o Bray Oil 814Z
- o Freon E6.5
- o JP-5
- o 3-(heptafluoroisopropoxy)-propyl trichlorosilane
- o 3-(heptafluoroisopropoxy)-propyl trimethoxysilane

The first four proved also to be ineffective plasticizers for Aflas/EPDM blends. JP-5 acted as a partial plasticizer by lowering the TR_{10} temperature 15°C.

The latter two materials were pre-reacted with the silica filler prior to incorporation into the compound. The intent was to coat the dried filler with the silanes to provide pendant heptafluoroisopropoxy groups to sorb into the Aflas/EPDM structure and lubricate the polymer blend for improved low temperature properties. This method also did not provide for an effective low temperature plasticizer.

Several questions remain unanswered which could provide the basis for a follow-on study:

1. Are Zetpol polymers more stable than conventional nitrile polymers as initial testing indicates. (Testing would involve JP-5 containing high levels of naturally "grown" peroxides).
2. Despite efforts to "grow" peroxides in NFP-14 identical to the procedure used for successfully "growing" peroxides in NFP-2, a peroxide level greater than 40 ppm could not be reached. A detailed analysis of NFP-14 would indicate what leads to its effective resistance to peroxide growth.

3. Di-t-butyl peroxide proved to be an ineffective referee; if such a referee could be found, a possible quality control specification could be devised for qualifying seal compounds. Therefore, various peroxides would be selected for addition to JP-5. Degradation of MIL-P-83461 compounds in this referee fluid will be compared with degradation of an identical compound in JP-5 containing "grown" peroxides.
4. Further exploration into synthesis of vinyl-terminated CTFE is needed to determine if this would be an effective plasticizer for Alfas:EPDM blends. It is speculated that the bulky chlorine atom present on CTFE is responsible for its plasticizing action. This may be why the structures evaluated this quarter did not provide the anticipated results.
5. Nitrile degradation is independent of aromatic concentration between 5 and 25% w/w. A study is needed to determine the effect of aromatic concentration between 0 and 5% w/w. It may be that 5% w/w is a critical concentration resulting in zero order kinetics.

1.4 SUMMARY OF THE LUBRICITY TASK

The problem of poor lubricity fuel emerged in the early 1970's as less desirable crude oil stocks were subject to severe refining processes, tending to remove those impurities which provide natural lubricating properties to fuels. Such properties are necessary for the survival of fuel handling hardware dependent on the lubricity of the fuel itself for survival. The most sensitive component is the fuel pump. There are instances recorded of fuel pump seizure leading to loss of aircraft and human life.

The problem is exacerbated by the absence of lubricity among the properties called out in JP-5 military specifications. Such a specification is absent for historical reasons, late recognition of the problem, and for technical reasons, failure of the fuel community to agree on a reliable laboratory test.

Some relief is provided by the specification for corrosion inhibitor as a fuel additive, since corrosion inhibitors are also synergistic lubricity enhancers. However the pilot must still depend on an accidental side effect of corrosion suppression to avoid fuel pump seizure. Some recent Air Force experience in qualifying shale derived fuel showed that careful cleaning of fuel storage and delivery facilities can result in removal of corrosion inhibitors from the fuel subsequently transported by these facilities and consequent pump failure.

1.4.1 Lucas Tester Technology

The Lucas Dwell Tester is a well built testing machine manufactured and sold during the late 1960's by the Lucas Aerospace Co. of Birmingham England. It's original mode of operation, measurement of a dwell number, was shown to be ineffective for the determination of fuel lubricity.

Mr. Carl Nau of TRW's Power Systems Division, Cleveland, Ohio, using the Lucas Dwell Tester as the basic machine, developed a lubricity tester measuring the friction factor as a drag coefficient between a weighted needle and a rotating disc. In turn, the drag was dependent on a film of fuel constantly replenished on the disc. This number is the boundary lubrication friction factor, a useful parameter in the theory of gear scoring. Details of the operation of the TRW/Lucas Tester, the flash temperature concept and its application in gear pump technology are contained in the main Lubricity Task report.

The data obtained in this program demonstrate that, used with care, the Lucas Tester yields reproducible friction factor data with a precision of better than $\pm 5\%$. Valid data are obtained for clay filtered isooctane, a standard for very harsh or zero lubricity fuel. The ball-on-cylinder machine (BOCM), now widely used in the lubricity community, can not operate with a harsh standard, hence the BOCM is difficult to "zero".

1.4.2 Evaluation of Corrosion Inhibitors

Using harsh isooctane as a baseline fuel, friction factor vs. concentration curves were obtained for each of the qualified corrosion

inhibitors. The data showed remarkable consistency from one product to another with Lubrizol slightly more effective than HITEC E-515 and UNICOR J slightly less. All the corrosion inhibitors caused reduction of the friction factor from about 0.7 down to 0.4 or 0.3 at concentrations under 1 ppm. With a concentration near 2 ppm the friction factors leveled off at values between 0.18 and 0.20 and remained in that band up to concentrations over 20 ppm. This effect is dramatically shown by the semi-logarithmic plots of friction factor vs. concentration presented in the detailed lubricity report. The plateau of friction factors starting at 2 ppm, is shown to be consistent with an estimate of the quantity of corrosion inhibitor (di-linoleic acid) required for monolayer coverage of the metal surfaces.

TRW/Lucas Tester studies, applied to an investigation of corrosion inhibitors, demonstrate 1) these compounds are very effective at extremely low concentrations, 2) the enhancement of lubricity does not increase beyond a concentration of 2 ppm and 3) lubricity distinctions among the commercial products are not important.

1.4.3 Evaluation of Sulfur Compounds as Lubricity Enhancers

Since removal of sulfur compounds during hydrotreating of crude oil has been assumed to contribute to the loss of lubricity accompanying refining, a study of the impact of various classes of sulfur containing species on friction factor was performed. These studies showed that sulfur containing species are not powerful lubricity enhancers. Compared to long chain organic acids they are about two orders of magnitude less effective.

2.0 ANALYTICAL CHEMISTRY TASK RESULTS

2.1 SEPARATION OF SULFUR COMPOUNDS via HPLC FRACTIONATION

The identification of sulfur compounds as minor species in the bulk of hydrocarbons requires their concentration prior to GC analysis. This pre-separation step is required even though we are using high resolution fused silica capillary GC and GC/MS. In fact, the GC/MS data show that more than one pre-separation step is probably needed to isolate the sulfur compounds well enough to permit unambiguous MS identification.

The first approach was to separate the fuel into different polarity fractions by high performance liquid chromatography (HPLC) on normal phase silica. This method separates the fuel into aliphatic/olefinic, alkylbenzene, alkylnaphthalene, and alkyl-anthracene fractions. It was hoped that the 2-ring alkylbenzothiophenes (alkyl BT), being more polar than the alkylnaphthalenes would be "retarded" one fraction and thus elute in the alkylanthracene fraction. This would increase the relative alkyl-BT concentration because alkylanthracenes are present at lower concentration than alkylnaphthalenes.

Fuels NFP-1⁽¹⁾, NFP-2 and NFP-3 gave four principal fractions (Figure 1) which were collected, concentrated, and analyzed by capillary GC and GC/MS. The GC was equipped with both HECD/S and FID detectors, with the effluent from the capillary column going to both detectors via a capillary splitter. Overlay of the HECD/S and FID chromatograms was done to pick out sulfur containing compounds in the FID runs, and, eventually, in the GC/MS runs.

The concentrated HPLC fractions were also analyzed by computerized GC/MS using both electron impact (EI) and methane chemical ionization (MeCI). Using 0.5 or 0.25 second MS scan times, GC/MS resolution was comparable to the GC runs.

2.1.1 GC Analysis of HPLC Fractions

Fused silica capillary GC with simultaneous detection by FID and HECD/S has proved useful in identifying which FID peaks contain sulfur. However, the

⁽¹⁾See Appendix A for a brief description of NFP fuels.

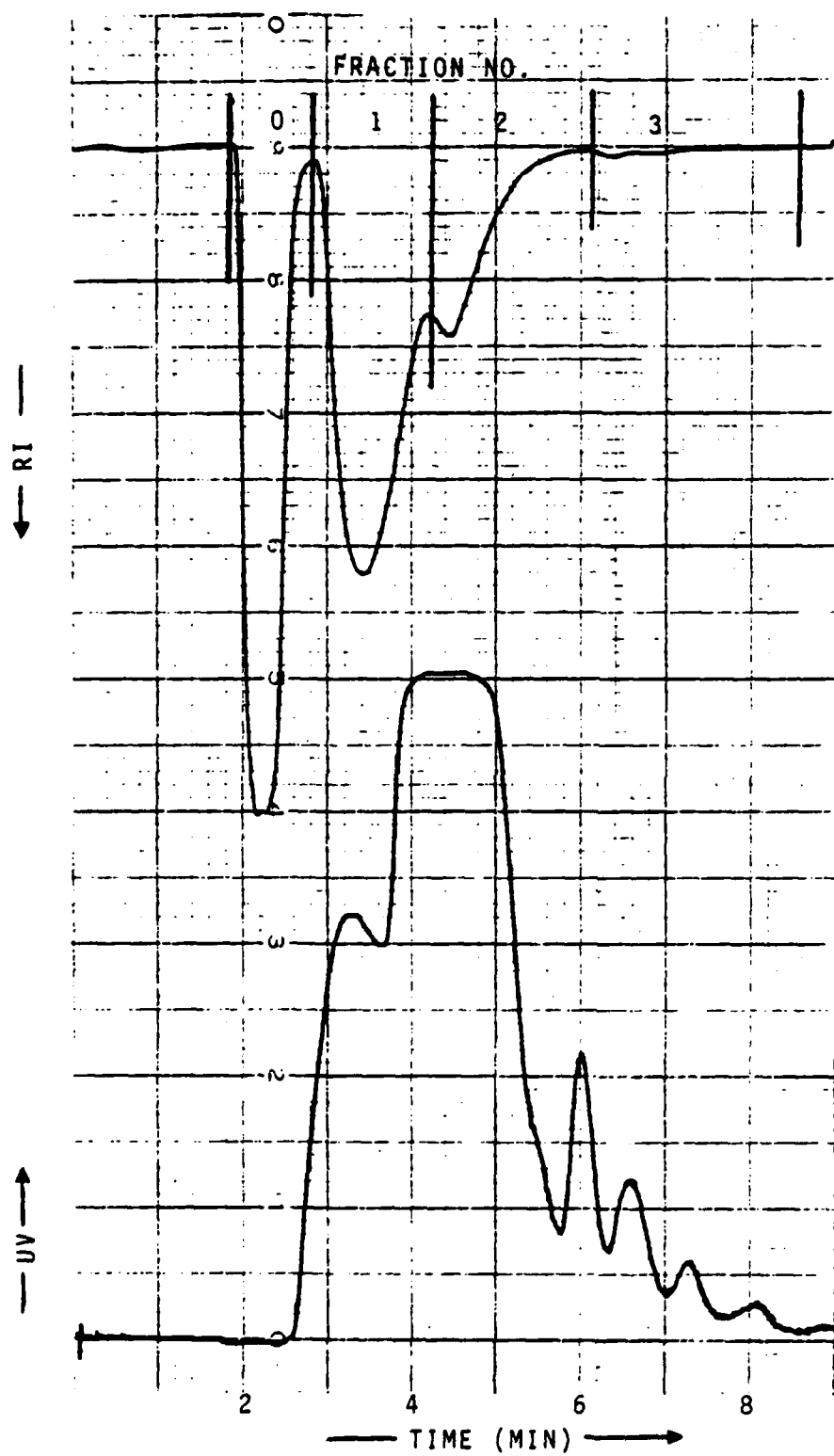


Figure 1. HPLC Chromatogram of NFP-1 on Silica With Hexane Mobile Phase

extreme sensitivity of the HECD/S coupled with its high discrimination against hydrocarbons can falsely lead one to believe that the speciation task is easier than it seems. The FID and HECD/S chromatograms for as-received NFP-3, and HPLC fractions 0-3, are presented in Figures 2-6. The chart speed in these runs was a fast 4 cm/min to simplify matching of compounds that give both FID and HECD/S responses. Some of the HECD/S peaks are offscale, as it was not always possible to estimate the concentration of sulfur compounds prior to GC analysis. GC resolution is quite good, without significant tailing of the polar compounds from the later HPLC fractions.

2.1.2 GC/MS Analysis of HPLC Fractions

GC/MS analysis of HPLC fractions 0-3 (See Figure 1) of NFP-3 is discussed below.

A) Fraction "0"

This HPLC fraction is transparent to UV down to approximately 220 nm. The HECD/S chromatogram shows no sulfur compounds, and GC/MS indicates saturated hydrocarbons as well as a few olefins. This paraffinic fraction accounts for ~80% of the original JP-5.

B) Fraction "1"

GC/MS shows that this fraction is composed primarily of alkylbenzenes. Overlay of the FID and HECD traces also reveals the presence of a large number of sulfur compounds, which although well resolved, are still obscured by high concentrations of alkylbenzenes. Even using computer assisted background subtraction techniques, it is very difficult to extract characteristic mass spectra from the welter of hydrocarbon ions.

C) Fraction "2"

This fraction contains primarily alkyl naphthalenes up to C₄, along with sulfur compounds. Even when the HECD/S shows sulfur compounds to occur in windows between the naphthalenes, they have not been detected in the GC/MS runs because of their low concentrations.

D) Fraction "3"

This fraction gives a very low RI response, but its several subfractions are clearly visible with the UV detector. GC/MS shows it to be primarily alkyl anthracenes/phenanthrenes, with some sulfur containing species. The extended UV chromophore in going from Fraction 1 (alkyl benzenes) to Fraction 3 (alkyl anthracenes) renders them more easily detectable by UV absorption, but their true concentration is more accurately reflected by the response of the RI detector.

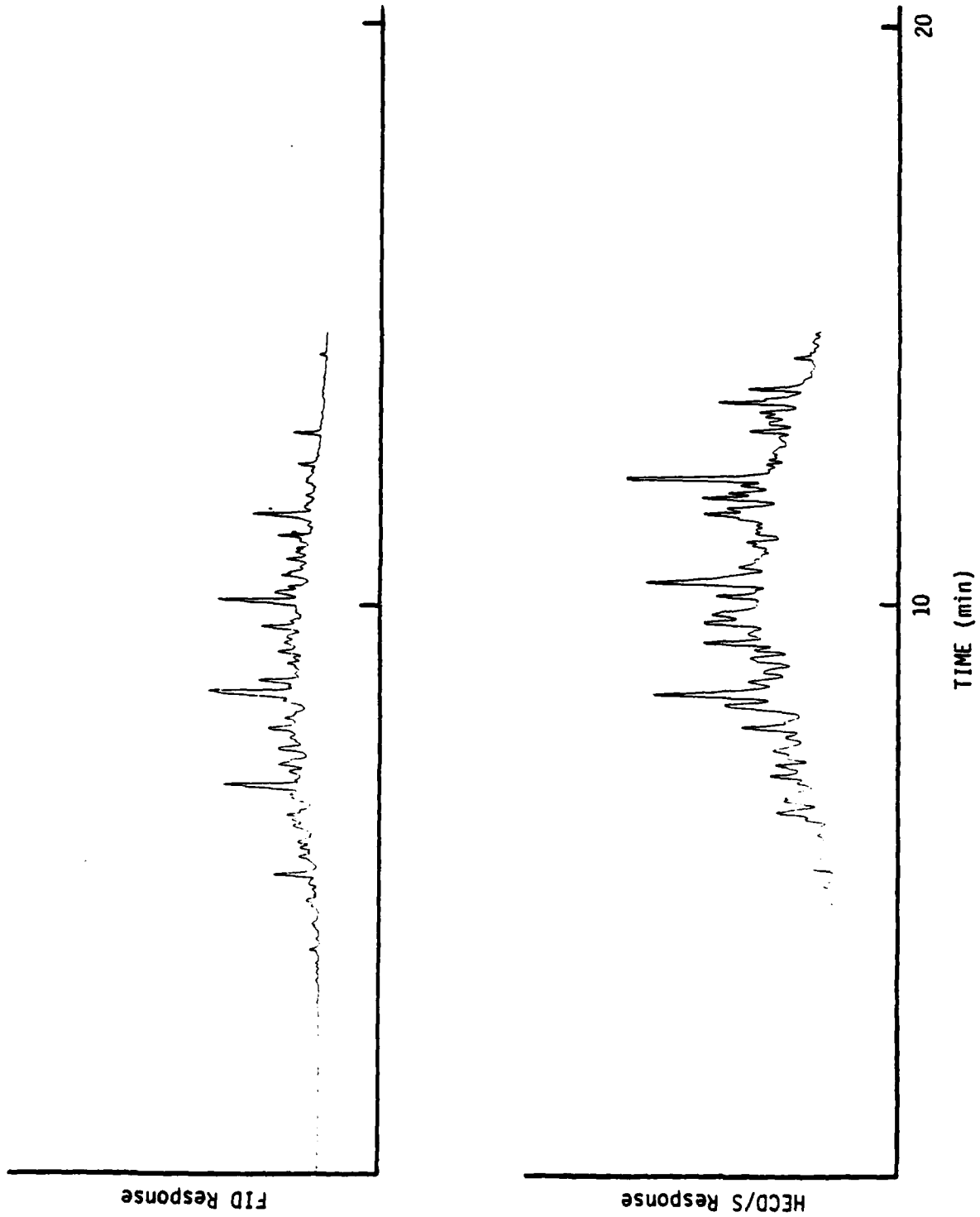


Figure 2. Chromatograms of NFP-3 As-Received.

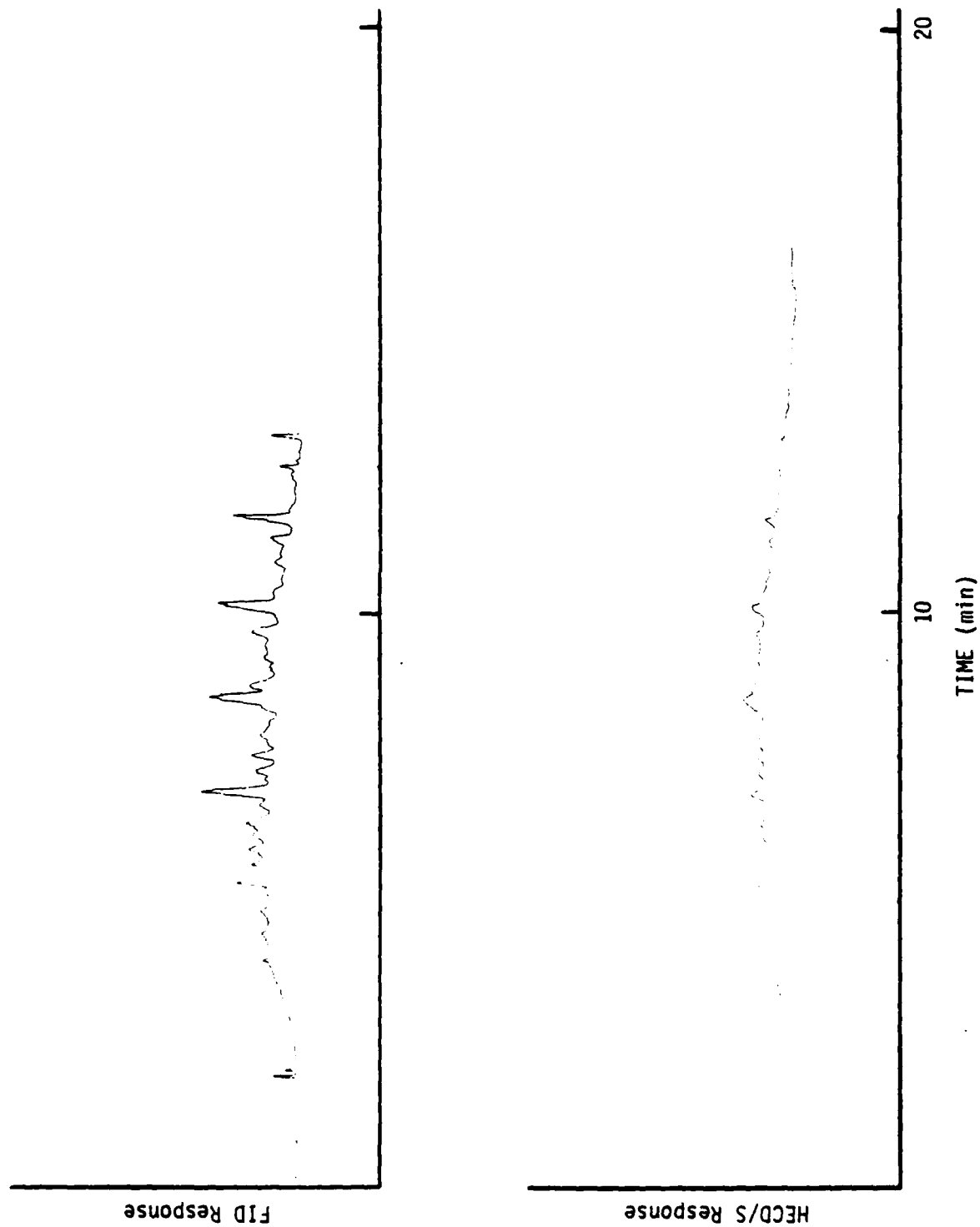


Figure 3. Chromatograms of NFP-3, HPLC Fraction 0

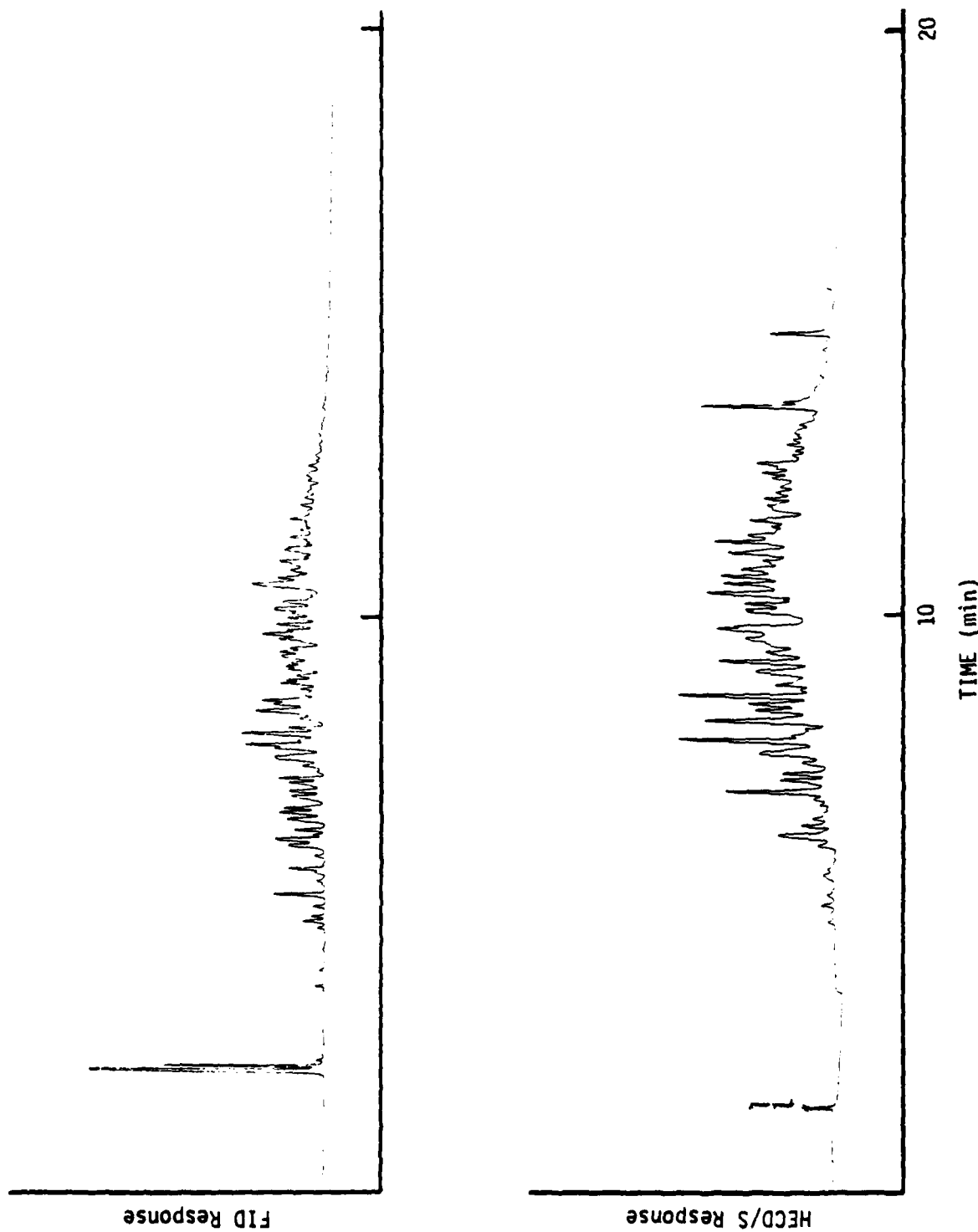


Figure 4. Chromatograms of NFP-3, HPLC Fraction 1

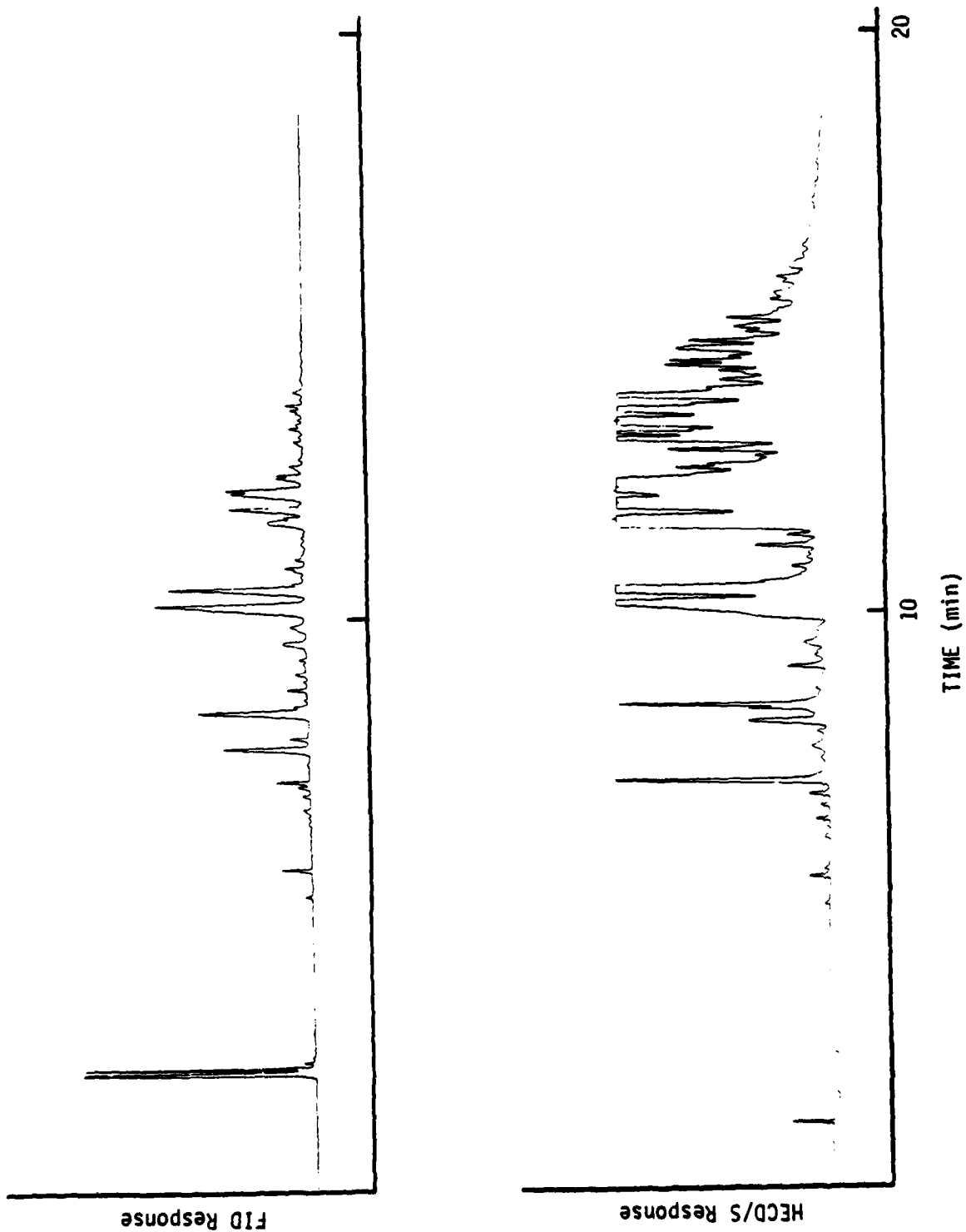


Figure 5. Chromatograms of NFP-3, HPLC Fraction 2

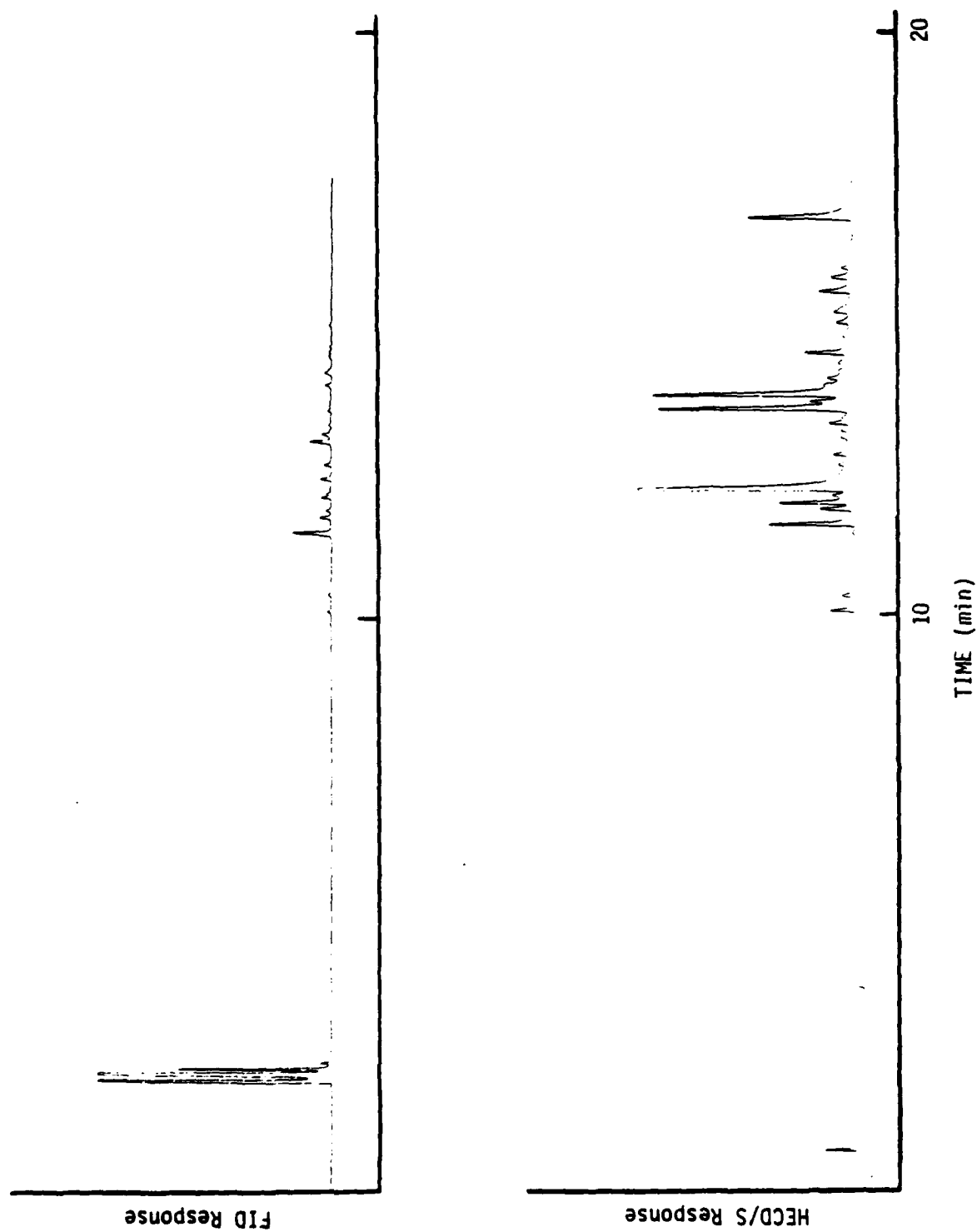


Figure 6. Chromatograms of NFP-3, HPLC Fraction 3

It is interesting to note that the sulfur compounds usually have higher boiling point ranges (i.e., longer retention times) than the hydrocarbons, even though they are both from the same HPLC polarity fraction.

2.1.3 Conclusions

HPLC was not effective in concentrating all, or even most of the sulfur compounds into one polarity fraction, so as to simplify compound identification by GC/MS. Computerized GC/MS search routines for C₁- and C₂-BTs and other sulfur compounds did not succeed in finding these compounds in any of the HPLC fractions. Sulfur compounds were not detected by GC/MS even in cases where the GC/HECD-S showed the sulfur compounds to appear in a hydrocarbon-free window.

2.2 SULFUR CLASS ANALYSIS

In order to develop a successful method for separating the sulfur compounds from the hydrocarbons, it was decided to first analyze the fuels for sulfur compound classes, and, based on these data, develop specific techniques for their isolation and identification.

2.2.1 Chemical Analysis for Sulfur Classes

The Bureau of Mines analysis procedure^(Ref.1) was used to determine sulfur class distribution in JP-5 fuels.

Briefly, mercaptans are removed by sequential treatment with metallic mercury and aqueous silver nitrate to give fraction L-3. This fraction is then treated with mercurous nitrate which removes aliphatic sulfides and disulfides to give fraction L-4. Fraction L-4 is then treated with mercuric nitrate, removing aromatic sulfides and thiophenes, to give fraction L-5. The flow diagram for this analytical approach is shown in Fig. 7. NFP-1 spiked with dibutyl disulfide (DBDS) dodecylmercaptan (C₁₂SH), dodecylsulfide (DDS), and dibenzothiophene (DBT) plus a sample of unspiked NFP-1 was run through this treatment scheme.

The spiked samples were run in order to monitor the efficiency of the treatment scheme on known compounds whose presence or absence could be readily monitored by GC. Spiked NFP-1 were run to check on whether any of the compounds in the fuel interfered with the removal reactions. The samples were examined by GC FID/HECD-S after silica gel HPLC fractionation to reduce the complexity of the chromatograms.

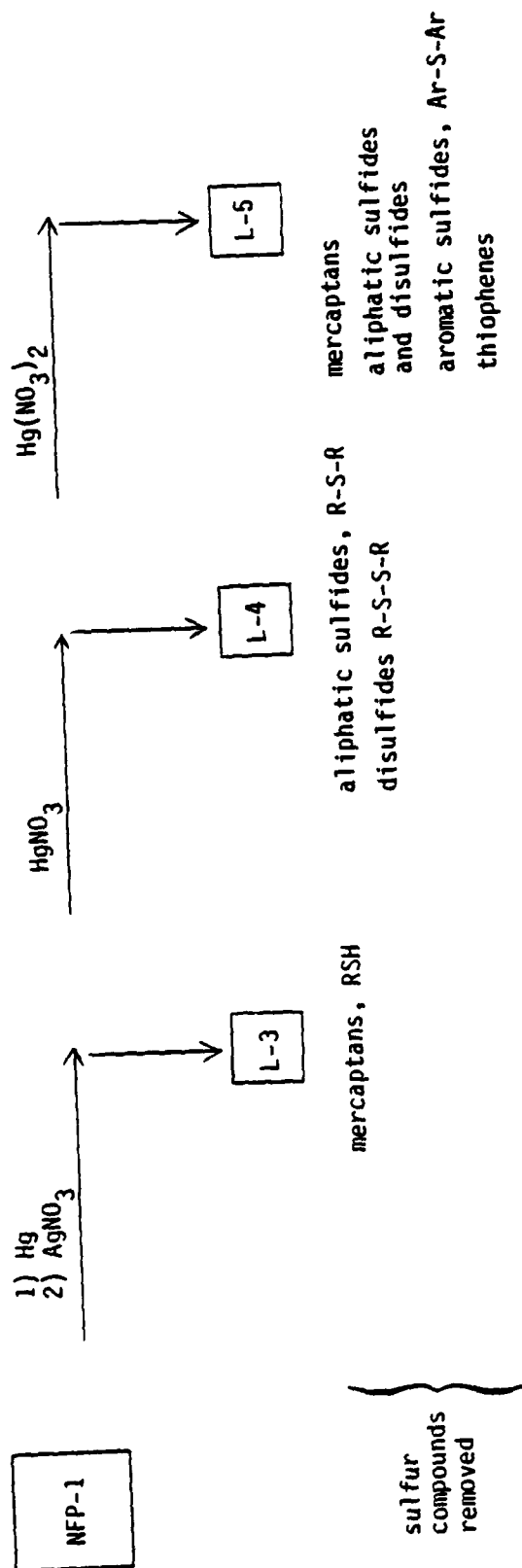


Figure 7. Flow Diagram for the Sulfur Class Analysis According to Reference 1.

Table 1 gives the results of the spiked runs, compared to the results expected according to Reference 1.

The GC/HECD-S chromatograms of HPLC fractions 1-3 of treated sample L-4, derived from unspiked NFP-1, were almost identical to those of the untreated fuel. Because DBDS, $C_{12}SH$, and DDS were all removed from spiked NFP-1 in fraction SL-4, it is concluded that the principal sulfur compounds in NFP-1 are BTs and DBTs, the only materials not removed by the chemical treatment procedures.

2.3 ISOLATION AND ANALYSIS OF BENZOTHIOPHENES BY THE LEE METHOD

The class analysis data were useful in revealing that most of the sulfur compounds were BTs. However, these are a very complex mixture of organosulfur compounds, spanning a broad boiling point range. Accordingly, a second approach was taken, involving the chemical separation and isolation of the BTs from the bulk of non-sulfur containing compounds. While the class analysis method relied on removing the sulfur compounds and leaving the hydrocarbons behind, this new approach involves removing the non-sulfur containing hydrocarbons and isolating the BTs.

This approach is an adaptation of the separation schemes of M. L. Lee^(Ref.2,3). A flow diagram of the Lee method is shown in Figure 8. Briefly, JP-5 is fractionated into four classes of compounds by liquid chromatography (LC) on alumina. The benzene eluate (A-2), containing the PASH and neutral polycyclic aromatic hydrocarbons (PAH), e.g., naphthalenes, is then oxidized with hydrogen peroxide (RXN 1), converting BTs to the corresponding sulfones and oxidizing some PAH and PASH at sites other than sulfur to quinones and hydroquinones. The unreacted neutral PAH are removed from the polar sulfones and quinone/hydroquinone fraction by LC 2, and the eluate reduced with $LiAlH_4$. This process converts the sulfones back to the original BTs, and reduces the quinones to hydroquinones. These latter materials, now being more polar than the PASH, are separated by LC 3 to yield PASH and HQ fractions. The PASH fraction, via oxidation of BTs to the corresponding sulfones (RXN 1), reduction of the sulfones back to the BTs (RXN 2), contains materials that were present initially in the JP-5. Oxygenated BTs, if they were originally present in the fuel, would be present in the oxygenated PAH fraction A4, and not make their way through RXN 1, and LC 2,

Table 1. Results of Sulfur Class Analysis of Spiked NFP-1
(According to Reference 1)

Fraction (1) Designation	Sulfur Compounds That Should Be Present (Ref. 1)	Spiked Runs Compounds Present	
		Hexane	JP-5
SL-3	DBDS	DBDS	DBDS
	—	—	—
	DBT	DBT	DBT
	DDS	DDS	DDS
SL-4	—	—	—
	—	—	—
	DBT	DBT	DBT
	—	—	—
SL-5	—	—	—
	—	—	—
	DBT	DBT	DBT
	—	—	—

(1) SL = "Spiked" Fraction L

The data in Table 1 shows that the expected compounds are removed in the treatment steps, and that other components in JP-5 do not interfere with these reactions. DBT should not be, and is not, removed by the treatment steps.

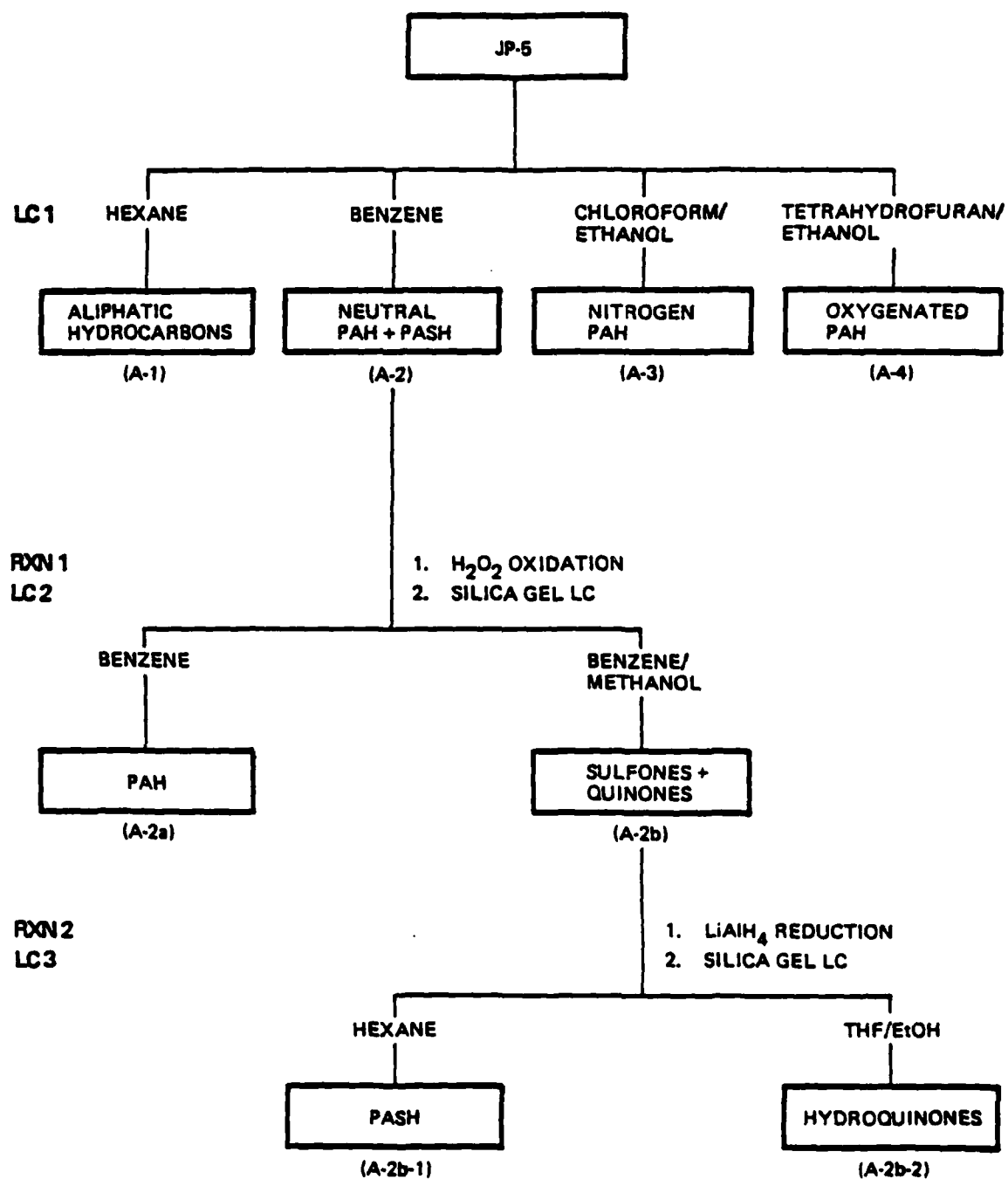
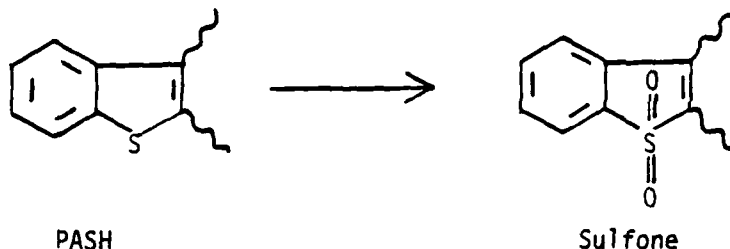


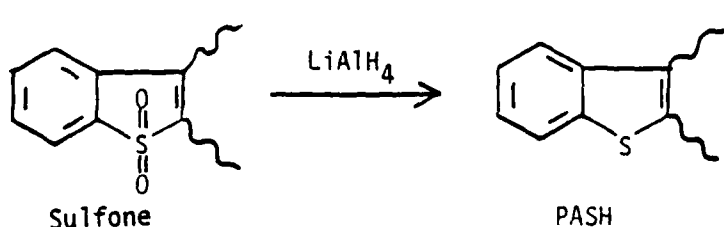
Figure 8. Flow Diagram of Lee Method

etc. The HQ fraction contains neutral PAH and PASH that were oxidized during RXN 1 at sites other than sulfur and were not fully reduced during RXN 2. Identification of these compounds would enable us to deduce their unoxxygenated structure, and more completely characterize the PASH.

The success of this method depends on 1) oxidation of PASH to their corresponding sulfones without oxidizing other parts of molecule.



2) Reduction of the sulfones back to the PASH without reducing other parts of the molecule. Thus, the original PASH are regenerated and GC/MS analysis of the reduced product gives valid data on PASH in the original, untreated fuel.



Fuels NFP-1, 2, 3, 6, 7, 10, and 11 were analyzed according to this method, and the results reported below.

In addition to isolating BTs, sulfur mass balance measurements were performed to check whether a significant amount of the sulfur compounds were lost during the LC and chemical treatment steps. Because all of the sulfur compounds are supposed to be isolated in LC-1 fraction A-2, and this fraction is the sole source of the PASH and HQ fractions, the total sulfur in the PASH and HQ fractions should be the same as that in the as-received fuel. Sulfur mass balance was checked using Parr bomb/ion chromatography and X-ray fluorescence, and the results reported in Section 2.4.

2.3.1. GC Analysis of the PASH and HQ Fractions

GC-FID/HECD-S analysis of LC-1 fractions A-1 through A-4 showed that sulfur compounds were present only in fractions A-2, confirming that the procedure Refs. 3-2,3 isolates all of the sulfur compounds in this fraction. Comparison of the sulfur and FID chromatograms for the PASH (Fig. 9 and HQ (Fig. 10) fractions of NFP-1 shows an excellent correspondence between traces. This means that almost every peak in the FID trace contains sulfur, or, conversely, there are no hydrocarbons present that will mask the sulfur compounds in GC/MS analysis.

2.3.2 GC/MS Analysis of the PASH and HQ Fractions

Portions of both PASH and HQ fractions were concentrated and analyzed by GC/MS on a 30M DB-5 fused silica capillary. Loss of GC resolution through scan digitization was minimized by acquiring data at a rate of 2 scans/second. BTs were identified by their MS fragmentation patterns, giving intense (30-100%) molecular ions, with alkyl losses at M-15, M-29, etc. Dihydro-BTs were identified by their molecular ions 2 amu higher than BTs. Losses of 44 (-CS) and 34 (H₂S) were sometimes observed.

2.3.2.1 GC/MS Analysis of the PASH Fraction

The capillary GC/MS chromatogram of the PASH fraction of NFP-1 (Figure 11) is qualitatively very similar to that obtained by capillary GC under the same conditions but using a Hall electrolytic conductivity detector in the sulfur mode (HECD-S), Figure 9. Peak assignments, along with GC/MS chromatogram and some representative mass spectra, are presented in Appendix B. Peaks were assigned as alkyl-substituted BTs on the following basis.

1. The corresponding HECD-S peak showed it to contain sulfur.
2. There was a strong molecular ion (30-100%) at the correct molecular weight (134, 142, 162..., for BTs; 136, 150, 164..., for dihydro-BTs).
3. Fragment ions indicated
 - a. loss of alkyl moieties (M⁺-15, M⁺-29, etc.)

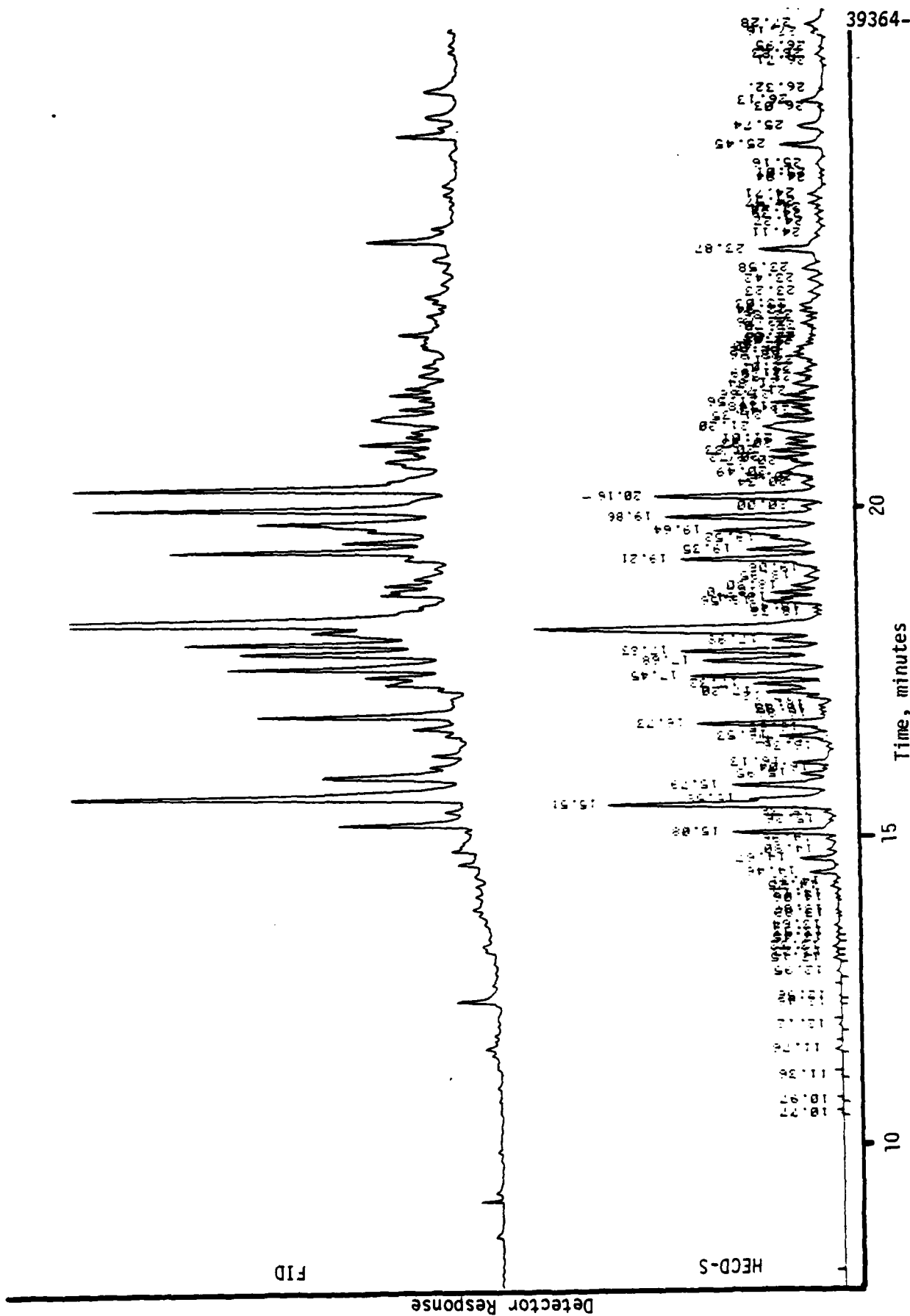
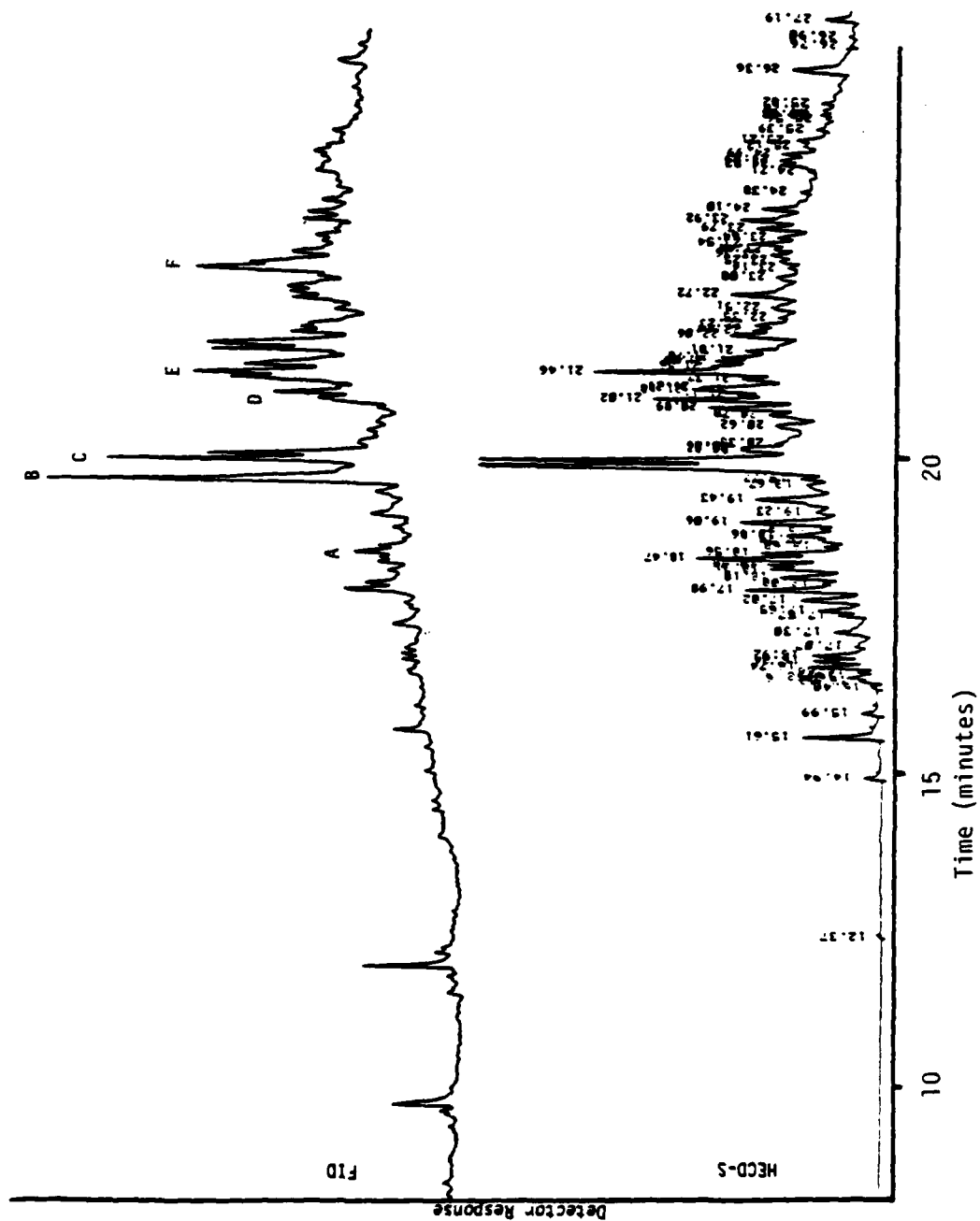


Figure 9. GC Chromatograms of NFP-1, PASH Fraction A-2b-1 (Scheme 1)

(a) FID

(b) HECD-S



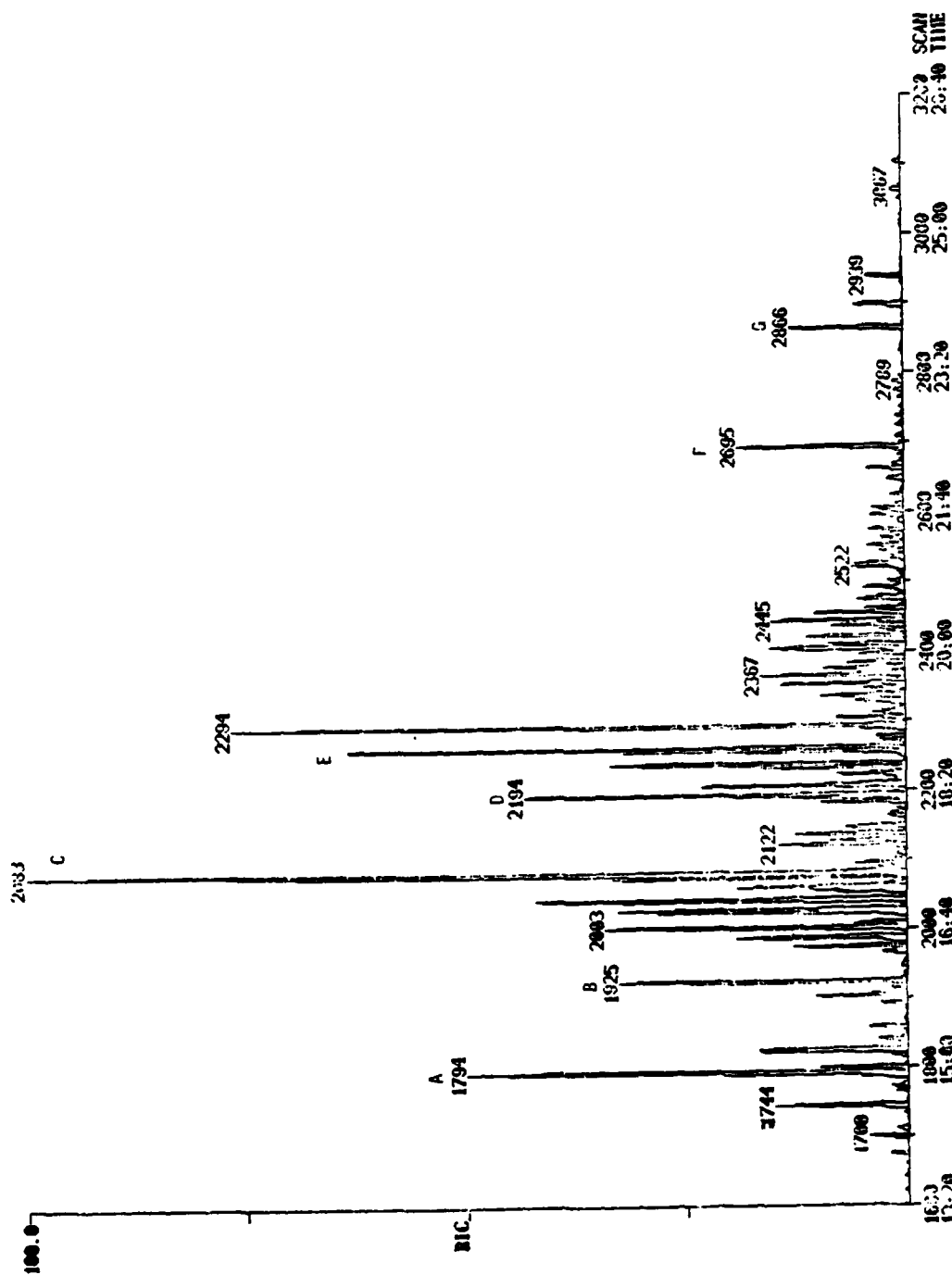


Figure 11. GC/MS Chromatogram of the PASH Fraction from NFP-1

- b. loss of what appear to be sulfur-containing neutrals such as HS ($M/z = 33$), and C_2H_4S (60)
- c. computerized MS library match for methyl-BT (scan 1794) and dimethyl-BT (scans 1989 and 2083).

Alkylated dihydro-BTs were assigned by their molecular ions ($BT + 2$) and fragmentation patterns.

Approximately seventy alkylated-BTs and dihydroalkyl-BTs were found by GC/MS. DBTs up to C_3 were also observed. Porter^(Ref.4) has reported the mass spectra (MS) of BT, its 2-, 3-, 4-, 5-, and 7-methyl-derivatives, and 2-ethyl BT, and concluded that:

1. the MS of 4-, 5-, and 7-methyl-BT are essentially identical
2. 2- and 3-methyl BT can be differentiated by the appearance of the CH_3CS^+ fragment at $m/e = 59$, although this ion is of low abundance
3. 2-ethyl BT shows a strong peak at $M^+ - 15$ and loss of 28 (C_2H_4) to give a strong ion at $m/e = 134$.

Many of the strong fragment ions can be rationalized by the formation of tropylium ($m/e = 91$, (1)), benzocyclopropenium ($m/e = 90$, (2)) and dihydrotropylium ($m/e = 89$, (3)) ions (or their open chain tautomers).

Preliminary examination of the mass spectra of the PASH fraction of NFP-1 shows:

1. the appearance of a fragment ion at $m/e = 59$ in some mass spectra (e.g., scan 2075, C_2 -BT, scan 2194, C_3 BT₃) indicating a 2-methyl substituent.
2. facile loss of CH_3 and C_2H_4 from a C_2 -BT, perhaps indicating the 2- C_2H_5 isomer (scan 2003).

Higher substituted BT give more complex spectra, in some cases indicative of branched alkyl substitution.

NFP-10 gave a much simpler mixture (Figure 12), composed of three C_1 -, six C_2 -, and six C_3 -BTs. No dihydro-BTs were seen. The mass spectra of all of the major BT peaks in NFP-10 compared well with those from the corresponding GC/MS peaks in NFP-1. The largest peak in both samples was assigned as a C_2 -BT (NFP-1, scan 2083; NFP-10, scan 2091).

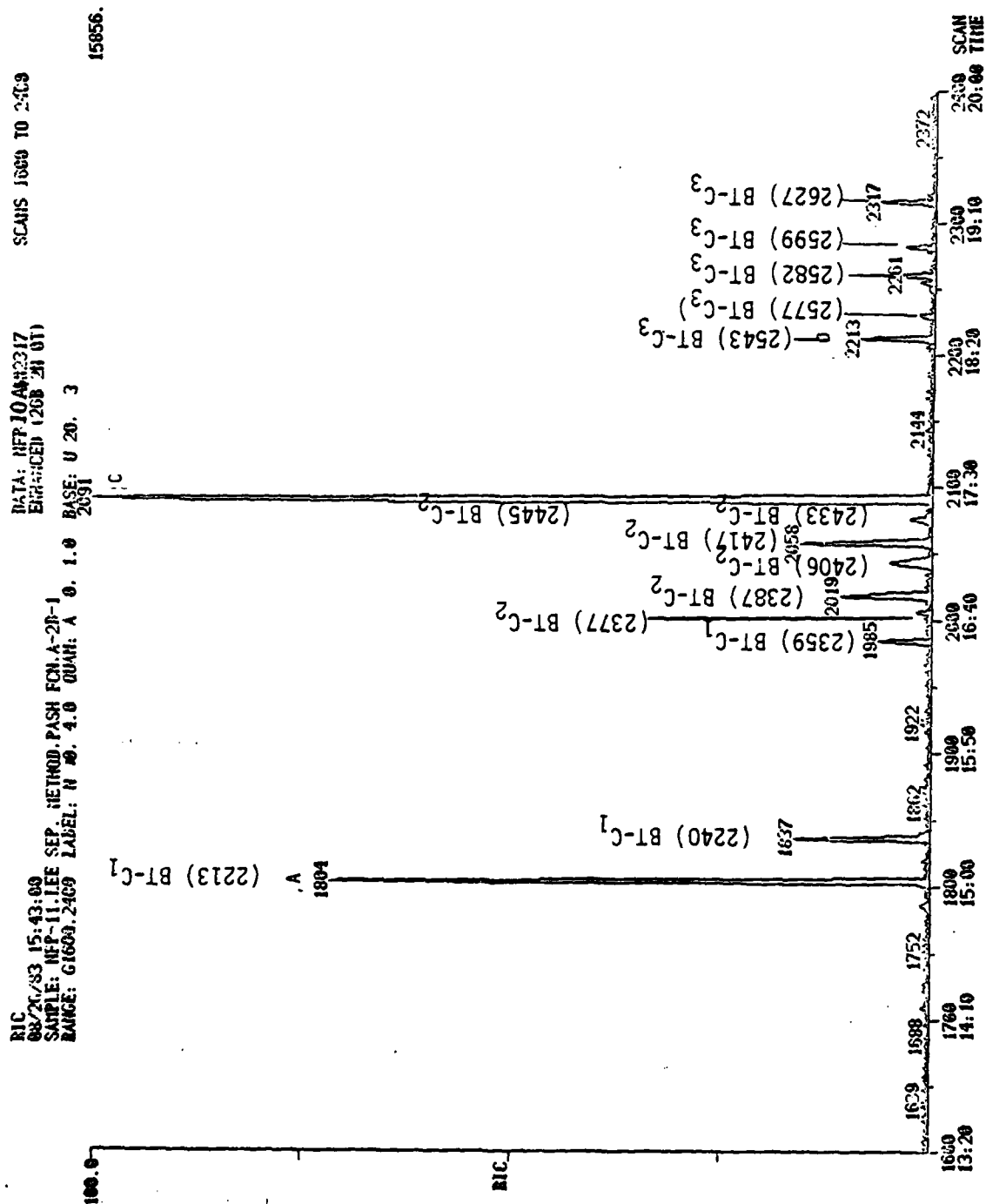


Figure 12. GC/MS Chromatogram of the PASH Fraction of NFP-10

2.3.2.2 GC/MS Analysis of the HQ Fraction

Both NFP-1 (Figure 13) and NFP-10 (Figure 14) gave extremely complex GC/MS chromatograms, with approximately 100 and 50 peaks, respectively. Peak-by-peak comparison between the NFP-1 HECD-S and FID runs, and the GC/MS run is not very instructive because of their complexity.. With some exceptions, most of the peaks contain sulfur. Some tentative non-sulfur assignments are: 2-methyl-(4), and 2,3-dimethyl-(5) 1,4-naphthoquinone (scans 2285 and 2535, respectively), trimethyl-1,4-naphthodquinone-(6), (scan 2788), and dimethylnaphthol(7), (scan 2756).

The formation of irreversibly oxidized sulfur compounds seen in the HQ fraction somewhat compromises the PASH isolation scheme. According to Fig. 8, these compounds were originally PAH and PASH that were oxidized at sites other than sulfur in RXN 2. If oxidation of these compounds in this fashion was an important process in fuel degradation, these materials would be isolated in fraction A-4 during LC-1 and not interfere with PASH and PAH oxidized in RXN 2. GC/HECD-S analysis of Lee fractions A3 and A4 showed that NFP-1 contained none (or only trace) amounts of oxidized sulfur compounds. Detailed MS analysis is beyond the scope of this effort, but the following features are worth noting.

- a. Many of the peaks did not give strong or discernible molecular ions, indicative, perhaps, of linear or cyclic aliphatic sulfur compounds.
- b. Hydroxy, dihydroxy, or quinoid alkyl BTs were not observed by searching the GC/MS run for molecular ions at 150, 166, 164, respectively, and their M + 14, 28...homologs.

2.3.3 Calculation of Retention Indices

Because of the complexity of the PASH and HQ fraction capillary gas chromatograms, it was decided to adopt a retention index (RI) system for keeping track of the individual GC peaks. This method, based on a system developed by Vassilaros and Lee^(Ref.5), calculates the retention indices of GC peaks bracketed by naphthalene (NP) and phenanthrene (PH) which is added to the samples as internal standards. These standards are assigned retention indices of 2000 and 3000, respectively and conveniently bracket PASH compounds from BT (RI = 2016) to DBT (RI = 2960).

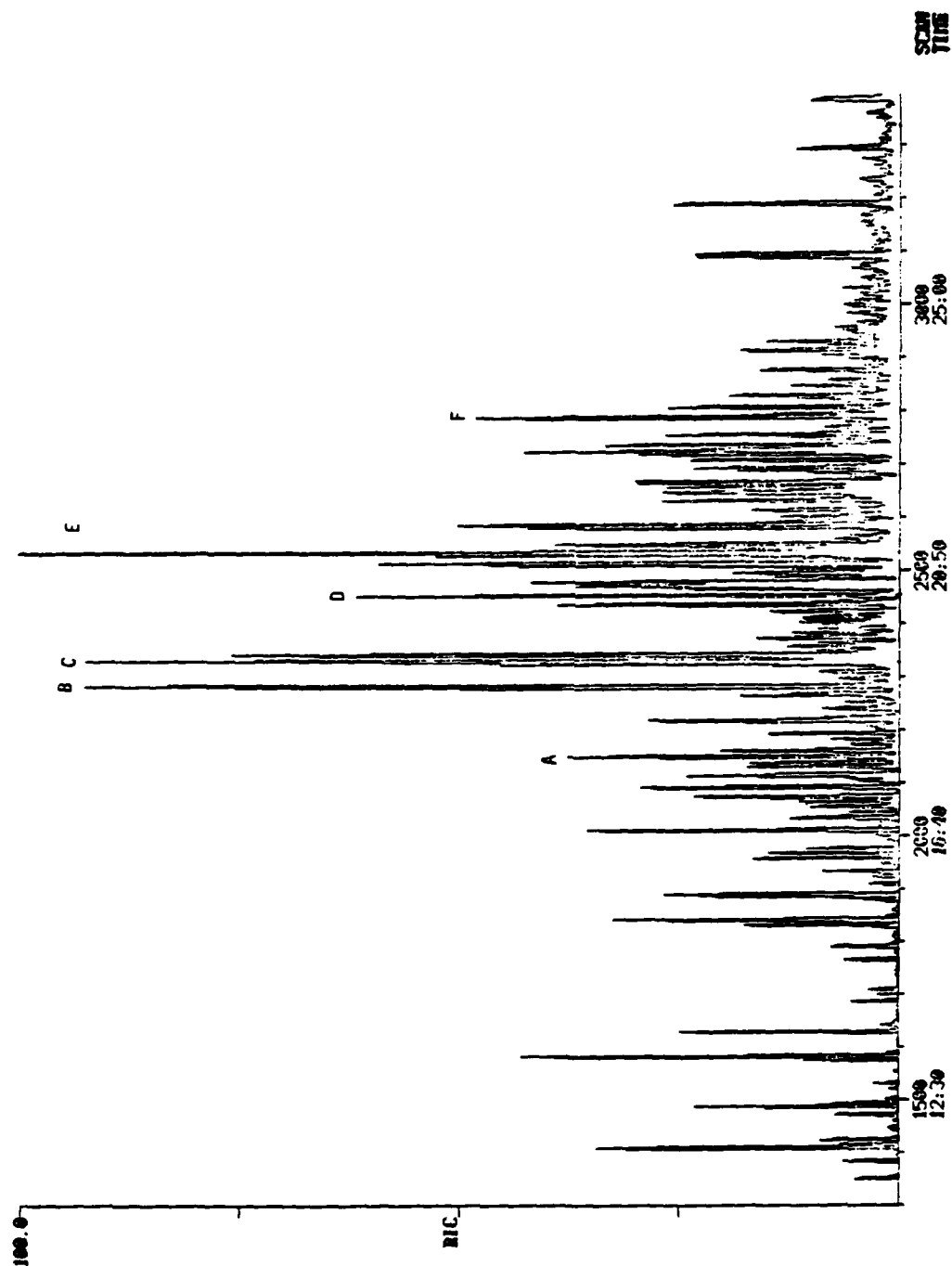


Figure 13. GC/MS Chromatogram of the HQ Fraction from NFP-1.

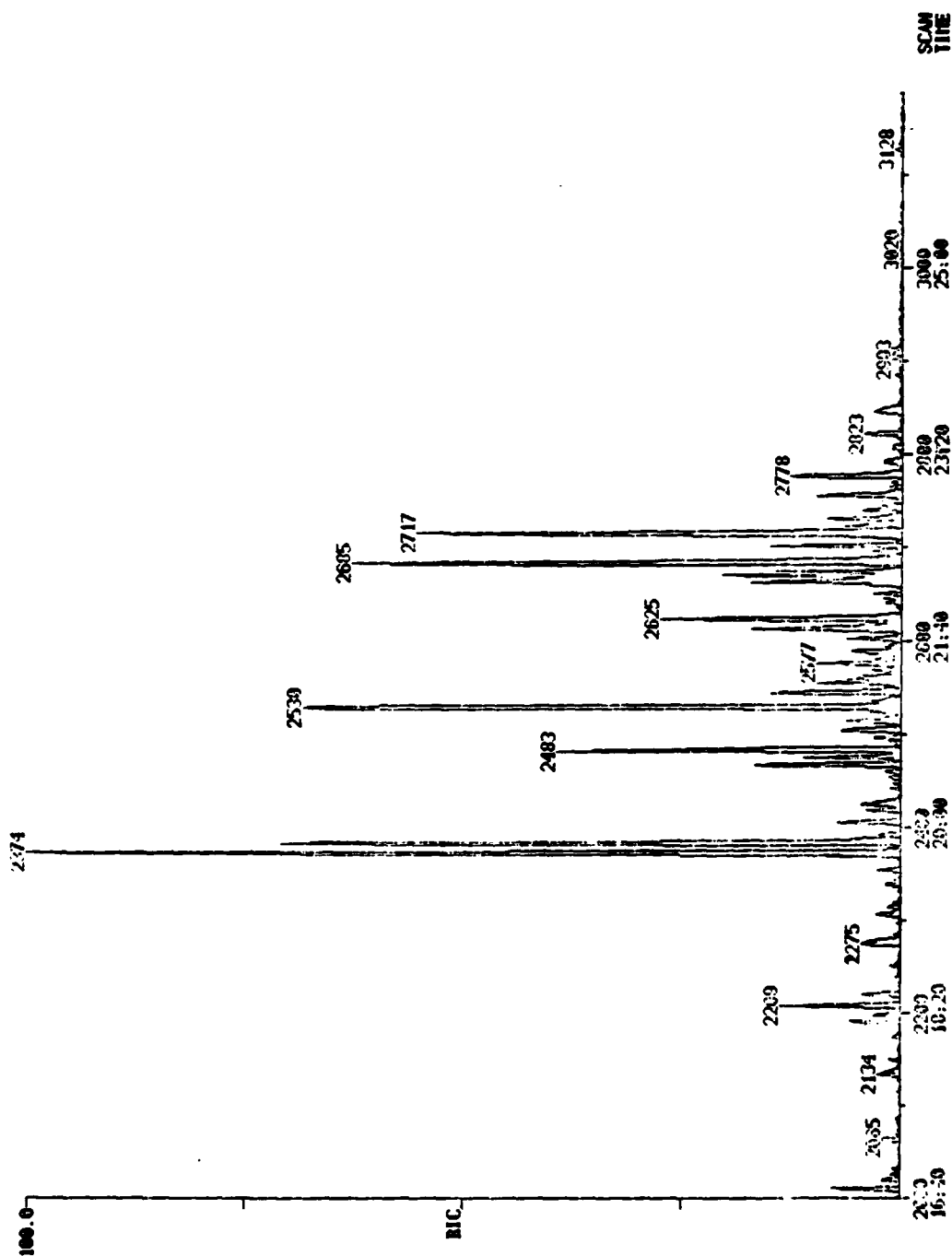


Figure 14. GC/MS Chromatogram of the HQ Fraction of NFP-10.

The RI of compound X is calculated as:

$$RI_X = 2000 + 1000 \left[\frac{T_X - T_{NP}}{T_{PH} - T_{NP}} \right]$$

where T_X = retention time of compound x

T_{NP} = retention time of NP

T_{PH} = retention time of PH

As long as all samples are analyzed on the same column under approximately the same conditions, the RI for each compound will not vary significantly, and compounds can be identified by a unique RI. This becomes very important in developing a data base on volatile sulfur compounds for the following reasons.

1. Variations in carrier gas flow velocity, capillary film thickness and condition, and temperature program rate will not significantly affect RI values. Without an RI system, these variations can lead to ambiguities in peak comparison and assignment.
2. Comparison of qualitatively different PASH chromatograms is not always possible without RI data because retention times are suspect.
3. Interlaboratory RI data can be readily compared.

RIs can also be used to estimate the boiling points of compounds of interest by comparison with normal hydrocarbons or other standards. A graph (Figure 15) of the RI of hydrocarbons from $n\text{-C}_{12}$ through $n\text{-C}_{16}$ shows the correspondence between RI and boiling point. A compound with an RI = 2500 would have a [hydrocarbon based] boiling point of 260°C . If suitable BTs of known boiling points were available, a BT-based RI/boiling point scale could be derived.

RI data for seventy-one compounds in GC/MS analysis of the PASH fraction of NFP-1, are presented in Table 2. Because some of the earlier runs did not contain the NP and PH internal standards, the RIs were calculated as follows using secondary standards. RIs of the peaks at 14.57 minutes ($\text{C}_1\text{-BT}$, RI = 2213) and 22.27 minutes (DBT, RI = 2960) were obtained from a GC/HECD-S/FID run of the PASH fraction of NFP-6 that contained NP and PH internal standards. Once the bracketing peaks of RI 2213 and 2960 were assigned, other RIs were obtained by interpolation between these compounds.

RIs of some of the important HECD-S and GC/MS peaks from several PASH fractions are presented in Table 3, showing excellent agreement for the same

Table 2. GC/MS Analysis and Retention Indices (RI)
of NFP-1 PASH Fraction

39364-6006-UT-00

Peak Number	Scan Number	GC Retention Time, min	RI	Assignment ⁽¹⁾	Peak Number	Scan Number	GC Retention Time, min	RI	Assignment ⁽¹⁾
1	1700	14:10	2135	BT(H ₂)	37	2385	19:52	2703	BT-C ₄
2	1794	14:57	2213	BT-C	38	2398	19:59	2714	BT-C ₄
3	1800	15:00	2218	BT-(H ₂)C ₁	39	2406	20:03	2720	BT-C ₄
4	1827	15:13	2240	Nph-C ₁	40	2423	20:11	2734	BT-C ₄
5	1841	15:20	2252	BT(H ₂)C ₂	41	2431	20:15	2741	BT-C ₄
6	1904	15:52	2304	BT(H ₂)C ₃	42	2438	20:19	2747	BT-C ₅
7	1925	16:02	2321	BT(H ₂)C ₂	43	2445	20:22	2753	BT-C ₄
8	1975	16:27	2363	BT(H ₂)C ₂	44	2456	20:28	2762	BT-C ₄
9	1989	16:34	2374	BT-C ₂	45	2463	20:31	2768	BT-C ₄
10	2003	16:41	2385	BT-C ₂	46	2467	20:33	2771	BT-C ₅
11	2029	16:54	2407	BT-C ₂	47	2475	20:37	2778	BT-C ₄
12	2044	17:02	2419	BT-C ₂	48	2492	20:46	2793	BT-C ₅
13	2075	17:17	2445	BT-C ₂	49	2502	20:51	2801	BT-C ₅
14	2083	17:21	2452	BT-C ₂	50	2522	21:01	2817	BT-C ₅
15	2122	17:41	2484	BT-C ₃	51	2534	21:07	2827	BT-C ₅
16	2128	17:44	2489	BT(H ₂)-C ₄	52	2539	21:09	2831	BT-C ₅
17	2138	17:49	2498	BT(H ₂)-C ₃	53	2545	21:12	2836	BT-C ₅
18	2148	17:54	2506	BT(H ₂)-C ₄	54	2551	21:15	2841	BT-C ₅
19	2164	18:02	2519	BT(H ₂)-C ₄	55	2564	21:22	2852	BT-C ₅
20	2184	18:12	2536	BT(H ₂)-C ₃	56	2570	21:25	2857	BT-C ₅
21	2194	18:17	2543	BT(H ₂)-C ₃	57	2576	21:28	2862	BT-C ₅
22	2207	18:23	2555	BT-C ₃	58	2596	21:38	2877	BT-C ₅
23	2224	18:32	2570	BT-C ₃	59	2606	21:43	2887	BT-C ₆
24	2233	18:36	2577	BT-C ₃	60	2649	22:04	2922	BT-C ₆
25	2239	18:39	2582	BT-C ₃	61	2683	22:21	2951	BT-C ₆
26	2257	18:48	2597	BT-C ₃	62	2695	22:27	2960	DBT
27	2262	18:51	2601	BT-C ₃	63	2709	22:34	2972	BT(H ₂)-C ₆
28	2278	18:59	2614	BT(H ₂)-C ₄	64	2739	22:34	2997	BT-C ₆
29	2294	18:57	2628	BT-C ₃	65	2751	22:55	3006	BT-C ₇
30	2305	19:12	2637	Nph-C ₃	66	2789	23:14	3038	BT-C ₆
31	2311	19:15	2642	Nph-C ₃	67	2866	23:53	3102	DBT-C ₁
32	2337	19:28	2663	Nph-C ₃	68	2899	24:09	3129	DBT-C ₁
33	2348	19:34	2672	BT-C ₄	69	2939	24:29	3162	DBT-C ₁
34	2354	19:37	2677	BT-C ₄	70	3107	25:53	3301	DBT-C ₂
35	2367	19:43	2688	BT-C ₄	71	3177	26:29	3359	DBT-C ₃
36	2377	19:48	2696	BT-C ₄					

(1) BT = Benzothiophene

H₂ = Dihydro

DBT = Dibenzothiophene

Nph = Naphthalene

C₁, C₂, ... = Methyl, dimethyl (or isomers thereof) substituted

Table 3. GC and GC/MS Retention Indices (RI)^a for Selected Polycyclic Aromatic Sulfur Heterocycles Separated by the Lee Method

Peak Assignment ^c	NFP-1 (GC)		NFP-1 (GC/MS)		NFP-3 (GC)		NFP-6 (GC)		NFP-7 (GC)		NFP-10 (GC/MS)		Average \pm S.D. RI
	T ^d	RI	T	RI	T	RI	T	RI	T	RI	T	RI	
A BT-C ₁	15.51	2213	14.57	2213	15.16	2213	15.47	2213	15.38	2213	15.02	2213	2213 \pm 0
A' Nph-C ₁	15.79	2238	15.13	2240	15.46	2240	15.76	2236	15.67	2236	15.18	2240	2238 \pm 1.97
C BT-C ₂	18.18	2451	17.21	2452	17.78	2446	18.06	2441	18.00	2445	17.25	2445	2447 \pm 4.13
D BT(H ₂)-C ₂	19.21	2543	18.17	2543	18.89	2544	19.17	2540	19.12	2545	18.26	2543	2543 \pm 1.67
E BT-C ₃	19.86	2601	18.51	2600	19.50	2598	19.78	2595	19.73	2600	19.01	2600	2599 \pm 2.14
E' BT-C ₃	20.16	2628	19.97	2627	19.82	2627	20.11	2624	20.08	2631	-	-	2627 \pm 2.51
G DBT-C ₁	25.45	3100	23.53	3100	25.16	3100	-	-	-	-	-	-	3100 \pm 0

^a Naphthalene = 2000, Phenanthrene = 3000 (Reference 4)

^b Peak numbering is consistent with Reference 3, Figure 4

^c BT = Benzo[thiophene]; (H₂) = dihydro; DBT = Dibenzothiophene, Nph = Naphthalene

^d GC Retention Time (minutes)

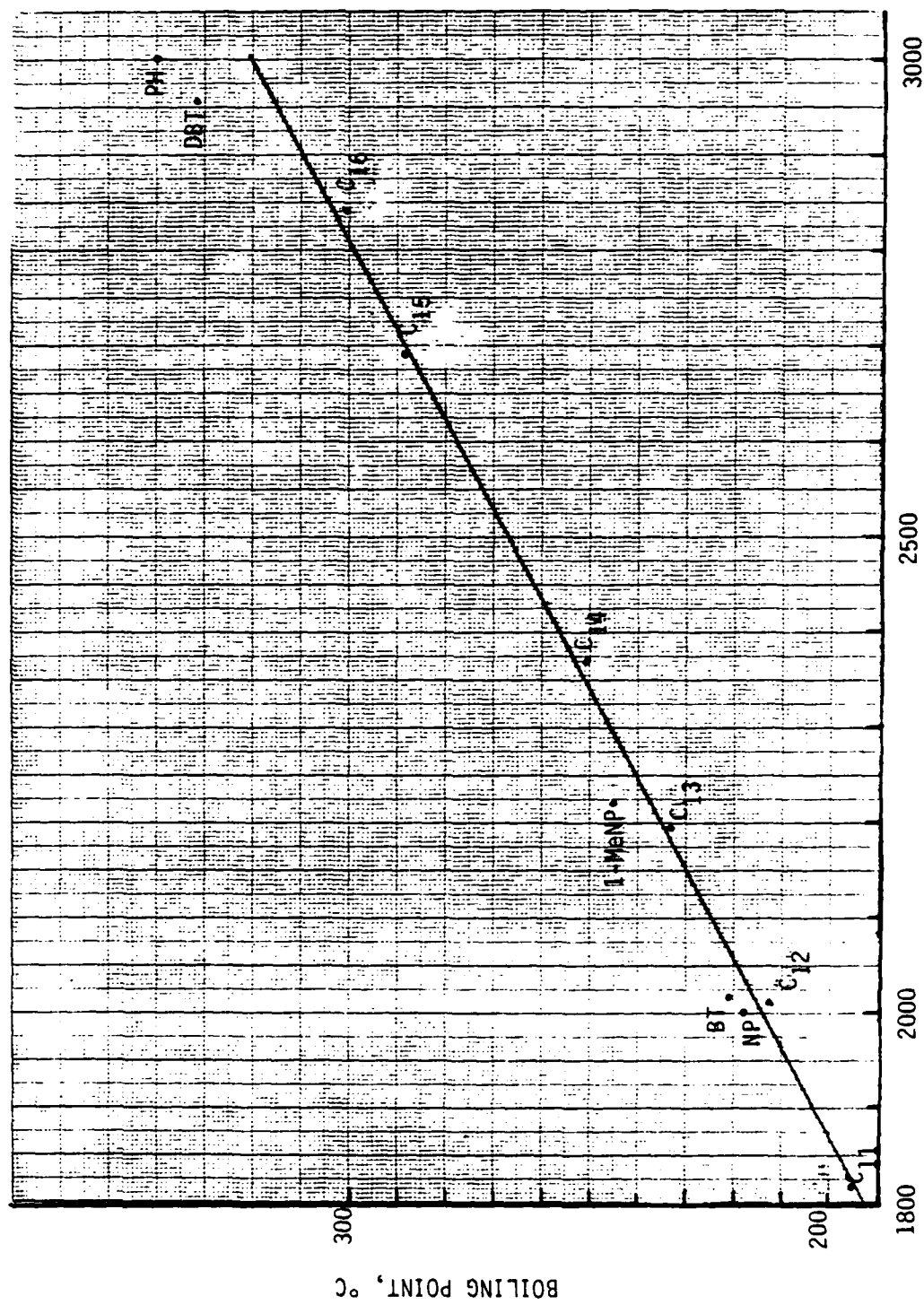


Figure 15. RI values versus boiling points of n-hydrocarbons (C_{xx}).
 NP = naphthalene, BT = benzothiophene, 1-MeNP = 1-methyl-naphthalene, DBT = dibenzothiophene, PH = phenanthrene.

compounds in different GC runs. For example, Peak D, has an RI equal to 2543 1.67, with elution times ranging from 18.17 minutes (NFP-1, GC/MS) to 19.21 minutes (NFP-1, GC). RI data for the PASH fractions of NFP-1, 3, 6, 7, and 10 are presented in Table 4.

Samples of the as-received fuels were also run to determine if the sulfur containing peaks in the PASH fraction can be seen in the original fuel, i.e., to confirm that the isolated PASH peaks are not experimental artifacts. Ten percent solutions of as-received NFP-1, 2, 3, 6, 7, 10 and 11 in heptane were analyzed by simultaneous GC/FID/HECD-S. Dithiane (DT, $C_4H_8S_2$) PH, and NP were added as internal standards: NP and PH for generation of RI data, and DT as a secondary retention time standard and marker peak in the HECD-S runs. Because these mixtures were so complex, it was not always possible to see NP in the FID or HECD-S runs. Consequently, a series of calibration runs were made with a mixture of DT, NP and PH yielding an RI for DT of 1746 \pm 4. RIs were then calculated based on interpolation between DT (1746) and PH (3000). PASH peaks that fall within \pm 4 RI units of those in the as-received fuels are starred(*) in Table 5. The number of these corresponding peaks varied from fuel to fuel, and the data are summarized in Table 6.

Table 6. RI Correspondence Between As-Received and PASH Fractions

<u>Fuels</u>	<u>Corresponding^a Number of PASH Peaks</u>	<u>Total Number of PASH Peaks</u>	<u>% Correspondence</u>
NFP-1	14	60 ^b	23
NFP-3	12	31	39
NFP-3 ^c	8	21	38
NFP-6	14	22	64
NFP-7	1	18	6
NFP-10	6	15	40

^aWithin \pm 4 RI units

^bFrom GC/MS run, Reference 3, Table 2 (p 19)

^cDuplicate run

(1) The PASH fraction of NFP-2 and 11 contained very small amounts of sulfur compounds and no meaningful RI data could be derived.

The percent correspondence between the PASH samples and as-received fuels is generally below 50%. These low values can be due to several factors, not

Table 4. RIs of the PASH Fraction of Sample Fuels by GC/HECD-S

RI	NFP SAMPLE DESIGNATION					
	1	3	5 ^Q	6	7	10
2000		2022	2017	2022*		
2100	2175*					
2200	2213 2218 2252*	2213* 2240*	2211* 2236*	2210 2236*	2213 2236	2213* 2240
			2288*			
2300	2304* 2321*		2330 2351	2316*		2359
	2363 2374* 2385*	2378* 2387	2384	2384	2388	2377* 2387*
2400	2407* 2419 2445* 2452	2408* 2419* 2433* 2446*	2403* 2414 2441*	2405* 2415* 2441*	2406* 2418 2445	2406 2417* 2433 2445*
	2484* 2489 2498* 2506 2519	2487*	2482* 2492*	2483*	2487	
2500	2536 2543 2555*	2525* 2544* 2557	2537 2547	2540* 2553*	2545 2557	2543 2558
	2570 2577 2585* 2597*	2581 2598*	2575 2591*	2574 2595*	2581	2577 2582 2599*
2600	2601* 2614 2628	2627*	2620	2624*	2600 2631 2639	2627
	2672 2677 2688* 2695 2703	2661 2679 2688 2698	2652 2679	2659* 2677* 2688	2666 2682 2692	
2700	2714 2720 2734 2741 2747 2753 2762 2768 2771 2778	2721 2735 2753 2776	2713 2730	2718*	2724	
2800	2793 2801 2817 2827 2831 2836 2841 2852 2857 2862 2877 2887	2791 2819 2830 2861 2879		2791 2818 2879		
2900	2922 2951 2960 2972				2968	
3000	2997	2993				

* Indicates RIs (within ±4 units) also found in as-received sample (Table 2).

Q Duplicate runs.

Table 5. RI Values of Sulfur Compounds in As Received Fuels by GC/HECD-S

	NFP SAMPLE DESIGNATION									
	1	1 ^a	3	3 ^a	6	6 ^a	7	10	10 ^a	11
2000	2029	2032	2035		2025			2032		2027
	2051	2054			2050			2052	2057	
	2056		2064		2060					2060
		2079	2088	2084	2083			2083	2080	2084
	2099	2097	2106		2099			2099	2100	2104
2100	2111	2110	2119	2114	2116		2115	2112	2110	2115
	2135		2143	2136	2135	2131		2136	2132	2137
	2152	2152	2158	2154	2154		2155	2151	2152	2159
	2169	2174	2176		2170			2170	2173	
	2185				2186	2182		2186	2178	2186
	2193	2194	2192				2193		2192	
2200	2205	2208	2202		2205			2207		2202
			2213	2210		2221			2210	
	2231	2230	2239	2238	2234			2232	2233	2233
									2245	2248
	2251							2250		
	2264	2268								
	2270			2270	2272		2270	2273	2273	
					2286				2288	
	2293		2291		2296			2292		
2300	2310	2306					2307			
	2318	2312		2312	2319			2316	2310	
			2323						2333	
			2340						2349	
			2364		2360			2357		2359
	2371	2371	2378	2375	2372			2371	2371	2372
		2385								
2400		2403	2407	2405	2402		2405	2400		
					2414	2418		2414		
			2420		2428			2428		
		2439	2434					2439		2433
	2441		2446	2443	2442	2442			2441	
		2467	2464		2461		2469	2459	2460	2464
		2481	2486		2484			2489		
2500		2497		2490						
			2525		2523					2523
			2542		2538					
		2552			2553					2571
					2567			2564		
2600	2598	2594	2598	2595	2594			2595	2594	
		2621	2626		2624	2623	2616		2617	
					2638	2645				2647
		2664			2657					
		2687			2677			2688		
2700					2715			2708	2708	2693
					2755					

^a Duplicate runs.

all of which relate to whether the PASH peaks are actually present in the as-received fuels. First, the GC chromatograms of PASH and as-received fuels are quite complex. Depending on the peak triggering sensitivity and area reject settings of the electronic integrator, the chromatogram can give anywhere from 50 to 150 peaks. Usually, peaks with area-% values of 1% or higher were selected for RI calculation, although in cases like NFP-2 and NFP-11, the low concentration of sulfur compounds, either in the as-received or PASH fraction, makes even this simple criterion somewhat useless. Unfortunately, there is no way to verify, e.g., by GC/MS, that all of the larger "as-received" sulfur HECD-S peaks are indeed sulfur compounds. Second, the boiling point and RI range derived from the PASH fraction is usually higher than that of the as-received fuel. It is not known whether this is due to chemical reactions in the Lee Separation Method that generate higher molecular weight materials, or to losses of low molecular weight compounds during this process. Our proposed study (Ref. 7) to separate sulfur compounds by an all-chromatographic method (eliminating the possibility of irreversible oxidation or rearrangement reactions) should help answer this question of the correspondence of isolated sulfur compounds.

2.4 SULFUR ANALYSIS

Sulfur analysis was performed to determine whether there were losses of sulfur compounds in the Lee method during the chemical reaction and LC steps. The amount of sulfur in the as-received fuels was compared with that in the PASH and HQ fractions: ideally, the sulfur in the combined Lee fractions should add up to that in the as-received fuels.

2.4.1 Parr Bomb Analysis

Initial sulfur assays were done by Parr bomb combustion (ASTM D 129-64) followed by analysis for sulfate ion by ion chromatography (IC). The mass balance data were not very good, with the PASH and HQ sulfur totaling from 64% to 144% of that in the as-received fuel (Table 7).

Subsequent examination of this method identified some likely problems, including 1) incomplete combustion due to spilling of the sample during bomb assembly or splashing during combustion, 2) incomplete conversion of sulfur to sulfate, 3) day-to-day variations in precision of the IC measurements.

Table 7 Sulfur Mass Balance Data

Sample	By XRF ⁽¹⁾				By Bomb/IC			
	As-Received	PASH	HQ	PASH + HQ (%) ⁽²⁾	As-Received	PASH	HQ	PASH + HQ (%)
NFP-2	N.D.	N.D. ⁽³⁾	N.D.	—	0.025	0.015	0.021	0.036 (144)
NFP-3	0.078	N.D.	0.053	0.053 (68)	0.078	0.036	0.041	0.077 (99)
NFP-6	0.035	N.D.	0.015	0.015 (43)	—	—	—	—
NFP-7	0.058	0.011	0.042	0.053 (91)	0.056	0.013	0.023	0.036 (64)
NFP-11	0.001	N.D.	0.014	0.014 (1400)	0.099	0.074	0.066	0.140 (142)

(1) Reproducibility of the Data is within $\pm 0.006\%$

(2) Percent of As-Received Sample

(3) Not detectable, below 0.001% (10 ppm)

Consequently, several other sulfur assay methods were considered and it was decided that x-ray fluorescence was the preferred method for these very low sulfur levels.

2.4.2 X-ray Fluorescence Analysis

A number of in-house discussions and telecons to local oil companies pointed to the analysis of low (10 ppm) sulfur levels in fuels using x-ray fluorescence (XRF) and counting times of several minutes. The XRF method has several inherent advantages that tend to make the data more reliable than the Bomb method, *viz.*

- 1) There is minimal sample preparation, hence less chance for inadvertant contamination by sulfur, losses of sample by spilling, etc.
- 2) Long counting times lend statistical confidence to the minimum detectability limits.
- 3) Calibration with the NBS fuel in toluene/heptane gave a linear plot ($r=0.999$) down to 10 ppm sulfur.

Accordingly, samples of as-received NFP-2, 3, 6, 7, and 11 were assayed by XRF per ASTM D2622-77 and the results compared to their PASH and HQ fractions. The following calibration and analysis procedures were employed.

- a) As-received fuel was assayed against standard dilutions of a high-sulfur diesel fuel (NBS sulfur in Diesel Fuel, 0.141% S) in 80/20 (v/v) heptane/toluene. This solvent approximates the C/H ratio in the distillate fuels, and minimizes dilution-based background errors.
- b) The PASH and HQ fractions, diluted in toluene, were assayed against standard dilutions of DBT in toluene. Because toluene comprises 99% of the dilute PASH and HQ samples, there is no C/H-based dilution error.

The XRF data are not an improvement over the bomb/IC assays (Table 7). Even though calibration curves of the NBS fuel in toluene/heptane allowed for the detection of 0.001% (10 ppm) sulfur in as-received fuels, several samples gave <0.001% sulfur, while the corresponding bomb/IC data showed up to 0.074% sulfur (NFP-11, PASH). At these low levels, it cannot be determined if the XRF method gave spuriously low readings or if some of the bomb/IC samples gave false high readings, perhaps because of inadvertant contamination during the rinsing and dilution steps. NFP-2, 3, and 11, all of which gave almost perfect (99% for NFP-3) or high sulfur mass balances (NFP 2 and 11) gave one or more <0.001% readings by XRF, rather indirect evidence of false positive sulfur levels by bomb/IC.

The finding of <0.001% sulfur in the PASH fraction of NFP-3 is puzzling, because GC/HECD-S data shows well defined progression of sulfur-containing compounds within the correct RI window. The bomb/IC assay, in contrast, shows this fraction to contain 0.036% sulfur. We cannot explain this discrepancy at the present time.

2.4.3 Mercaptan and Disulfide Analysis

Because mercaptans and disulfides were estimated to be present at low ppm levels, they were determined separately on 6 samples of JP-5 by the Exxon method (Ref. 7,8).

Solutions were promptly titrated after reduction and work-up to minimize decomposition. Mercaptans and disulfides are reported as wt-% sulfur from the titrations, assuming 32 g S/equivalent, i.e., one equivalent of silver nitrate per mole of mercaptan. The data for mercaptan and disulfide are reported in Table 8.

These values are very low compared to the BT levels in NFP-1 (0.16% S=1600 ppm) and would not be seen in sulfur assays done by difference.

Table 8. Mercaptan and Disulfide Analysis¹ of JP-5 Samples

Sample	Mercaptan, ppm	Disulfide, ppm	Total, ppm
NFP-1	9.4	2.3	11.7
NFP-3	3.4	10.4	13.8
NFP-6	1.9	1.5	3.4
NFP-7	4.5	2.2	6.7
NFP-10	4.7	2.9	7.6
NFP-11	0.47	5.4	5.9

¹ ppm sulfur, by weight, for JP-5 with a density = 0.82 g/mL

2.5 SIMULATED DISTILLATION

In addition to knowing the types and amounts of sulfur compounds in JP-5, it is useful to obtain information on the boiling point range of the sulfur species themselves. The boiling range of the sulfur compounds is not necessarily the same as the bulk fuel, and might be a sensitive function of refining methods or crude sources. Furthermore, the sulfur compound boiling range can affect hydrotreating and other fuel finishing processes.

Simulated distillation (SD) analysis was performed on JP-5 fuels and then PASH fractions using a capillary GC with FID or HECD-S detection, based on ASTM 2887. The as-received fuels were run by GC-FID/HECD-S, and the PASH fraction run by GC-FID only.

Because the PASH was analyzed by GC-FID, the "%-off" values reported are based on the weight-% of PASH compounds as hydrocarbons, not sulfur species. For these analyses, the simulated distillation curves using a FID or a HECD-S will be equivalent if the weight-% sulfur in each compound remains the same with increasing molecular weight. Since the weight-% of sulfur decreases in going to alkylated higher molecular weight compounds, the PASH/FID and HECD-S data will not be exactly equivalent and the HECD-S data should show higher %-off values at lower temperatures.

The SD x-axis temperature calibration is based on the boiling points of normal hydrocarbons, and other classes of compounds such as organo-sulfurs and aromatics may not track with this calibration, e.g., DBT, b.p. 332°C, boils about 17°C higher than its RI would indicate. These data should therefore be viewed as qualitative insofar as comparing the boiling point range of the sulfur compounds versus the hydrocarbon standards. However, sample-to-sample differences between the HECD-S SD curves reflect differences in their sulfur compound distributions. Table 9 reports the simulated distillation data for as-received NFP-1, 2, 3, 6, 7, 10 and 11 using both FID and HECD-S detectors, and PASH/FID data for NFP-1, 3, 10 and 11, with the HECD-S data giving a picture of the distribution of sulfur, not sulfur compounds as a function of boiling point.

The hydrocarbon (FID) data are very similar for all seven fuels examined, as would be expected for a distillate fuel with a specified boiling point range. The 50%-off values fall within 217-222°C, except for NFP-7 (229°C).

In contrast, the sulfur SD curves vary quite markedly, having a broader boiling-point distribution than the hydrocarbons, and giving different proportions of high and low boiling components. Based on the 50%-off temperatures, NFP-1 has the highest median boiling point for the sulfur compounds, and NFP-2 the lowest. Differences in the shape of the curves might indicate subtle differences in crude sources or refining techniques. The PASH fraction shows a higher boiling point range than the corresponding sulfur compounds in the as-received fuel as determined by HECD-S. This is also reflected by their generally higher RI range.

Table 9. Simulated Distillation Data on JP-5s

Sample	Temperature, °C, for Indicated %-Off						
	0.5	5	25	50	75	95	99.5
NFP-1							
FID (As Received)	142	170	197	218	239	271	307
HECD-S (As Received)	107	145	202	229	257	293	330
FID (PASH)	227	232	255	267	280	306	325
NFP-2							
FID (As Received)	145	175	202	221	239	258	279
HECD-S (As Received)	100	118	165	203	234	275	343
FID (PASH)	-	-	-	-	-	-	-
NFP-3							
FID (As Received)	152	176	200	219	240	266	296
HECD-S (As Received)	102	134	195	226	255	290	332
FID (PASH)	223	230	245	257	268	278	282
NFP-6							
FID (As Received)	149	174	201	222	244	273	299
HELD-S (As Received)	101	122	176	218	256	296	342
FID (PASH)	-	-	-	-	-	-	-
NFP-7							
FID (As Received)	151	178	206	229	250	279	306
HECD-S (As Received)	101	123	187	226	260	301	340
FID (PASH)	-	-	-	-	-	-	-
NFP-10							
FID (As Received)	141	170	203	217	233	252	279
HECD-S (As Received)	101	125	184	218	242	289	336
FID (PASH)	125	166	200	215	228	251	272
NFP-11							
FID (As Received)	139	168	196	218	239	273	319
HECD-S (As Received)	100	118	166	213	245	301	343
FID (PASH)	223	226	228	244	260	318	348

2.6 METALS ANALYSIS

Six NFP samples have been analyzed for metals by inductively coupled argon plasma by (ICAP), and the results presented in Table 10.

Table 10. Analysis of NFP Samples for Metals
by ICAP Concentrations in ppm

Metal ^a	NFP Sample					
	1	2	3	7	10	11
Sodium	0.8	2.0	2.3	10	2.7	1.7
Potassium	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Calcium	0.582	0.876	1.34	3.76	1.45	0.662
Magnesium	0.075	0.058	0.05	<0.04	<0.04	<0.04
Lead	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Vanadium	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003

^a Traces of boron and titanium were the only other elements qualitatively observed

All of the fuels contain less than 0.1 ppm of Mg, Pb, and V, with somewhat higher levels of Ca (0.5-3.8 ppm) and Na (0.8-10 ppm). The Na/Ca ratio was fairly constant, varying from 1.4 (NFP-1) to 2.7 (NFP-7).

3.0 EXPERIMENTAL

3.1 GAS CHROMATOGRAPHY

Tracor Model 560 GC equipped with an FID and HECD-S

Column: J&W Scientific 30 m 0.2 mm i.d., DB-5, helium carrier at 17 psi, 25.6 cm/sec (110°C), temperature programmed at 8°C/min from 50°C (2 min) to 280°C and hold (if necessary). $N_{eff} = 1990$ plates/meter, C_{13} , $k = 5.34$

Injector: J&W inlet splitter at 275°C; quartz flow inverting liner packed with glass beads deactivated at 200°C with 1:1 DMDCS:HMDs; split 30 ml/min

FID: 285°C, helium make up at 30 ml/min

HECD-S: Solvent: Methanol, flow control at 12 O'Clock

Reactor Temp: 850°C. Column vent left on to clear solvent FID peak.

Reaction Gas: Air, 50-100 ml/min, helium make up at 30 ml/min.

Data Processing: FID/HECD-S Channel: Spectra Physics 4000, FID plot, FID and HECD-S integration

HECD-S Channel: Hewlett-Packard 3385A Recording Integrator plot, redundant HECD-S integration.

3.2 GC/MS

(Dupont 321 With INCOS Data Handling System)

GC: Column: 30m x 0.25 mm i.d. J&W DB-5, helium carrier at 16 psi (27 cm/sec at 130°C). N_{eff} (C_{13} , $k = 11.3$,) = 3150 plates/meter

Injector: J&W inlet splitter, flow-inverting quartz liner packed with glass beads and deactivated at 200°C with 50:50 HMDs:DMDCS. Operated at 280°C, split at 30 mL/min

Temperature Program: 50°C (2 minutes) programmed at 8°C/minute to 280°C and hold

MS: Scan 55-450 amu at 0.5 seconds/scan

Jet: 250°C

Source: 225°C

Ionizer: 70 eV

3.3 HPLC

Samples were fractionated on a DuPont 850 HPLC fitted with a 25 cm silica column and eluted with hexane at 1 or 2 ml/min. Eluants were detected by sequential UV (275 nm) absorption and refractive index (RI) detectors.

3.4 SEPARATION and ISOLATION of the PASH and HQ FRACTION JP-5

LC-1

A 10 g sample of JP-5 was mixed with 50 g of neutral alumina (Fisher A950, 80-200 mesh) and added to the top of a glass column containing an additional 100 g of neutral alumina. The column was eluted with the following solvents to yield fractions A-1 through A-4.

<u>Solvent</u>	<u>Amount</u>	<u>Fraction</u>	<u>GC/HECD-S⁽¹⁾</u>
Hexane	333 mL	A-1	0
Benzene	833 mL	A-2	X
Chloroform (with ethanol preservative)	1166 mL	A-3	0
90% TH (UV Grade) + 10% ethanol	833 mL	A-4	0

(1) Analysis for sulfur compounds; Present-X, absent - 0

RXN-1

The benzene fraction, A-2, from LC-1 was reduced to approximately 25 ml using a Kuderna-Danish evaporator and added to 25 ml of glacial acetic

acid in a 100 ml 3-necked flask. Approximately 20 ml of 30% H_2O_2 was added dropwise over a 1 hour period and the mixture refluxed for 16 hours. The mixture was cooled and washed with five 50 ml portions of water. The water washings were back extracted with benzene, the benzene washed with 5 ml of saturated brine and reduced to 5 ml.

LC-2

The benzene extract was added to 5 g of 60-200 mesh silica gel (Fisher S-662, Grade 950) and the mixture gently blown with nitrogen to remove excess solvent. This mixture was added to the top of a column containing 15g of silica gel and eluted with 80 ml of benzene to yield fraction A-2a, unoxidized PAH. The column was then eluted with 1:1 benzene:methanol to yield fraction A-2b, oxidized PAH and sulfones.

RXN-3

Fraction A-2b was gently taken to dryness and dissolved in 25 ml of ethyl ether. This solution was slowly added to a suspension of 1 g of LiAlH_4 in 50 ml of refluxing ethyl ether. The mixture was refluxed for 2 hours, after which time water was slowly added to decompose the excess hydride. The ether was removed from the inorganic precipitate by decantation and filtration, and the precipitate washed several times with ethyl ether and methylene chloride. The combined ether/methylene chloride solution was gently evaporated to dryness.

LC-3

The product of RXN-3 was taken up in a few ml of hexane and added to 1 g of silica gel. The hexane was removed and the silica gel added to the top of a column containing 9 g of additional silica gel. The PASH were eluted with 250 ml of hexane to give fraction A-2b-1, leaving a brown layer at the top of the column. This material was stripped by elution with 1:1 ethanol:THF to yield hydroquinones and other polar materials, fraction A-2b-2.

3.5 SULFUR ANALYSIS

3.5.1 Mercaptan and Disulfide Analysis

Disulfide Analysis

1. Reduction:

To 20 ml of a solution of 2% w/v NaBH_4 in diglyme add 5 ml JP-5 followed by dropwise addition of 10 mL of 10% w/v of AlCl_3 in diglyme. Attach a condenser and stir for 3-1/2 hours. Cool the flask in an ice bath and add sequentially 20 mL 1M NaOH, 10 ml 3M HNO_3 and 6 M NaOH to a phenolphthalein endpoint. Add 10 ml of "magic solvent" (see below), 10 mL conc. NH_4OH and titrate with 0.002 M AgNO_3 standardized against sodium bromide solution.

Magic Solvent

Dissolve 5 g sodium acetate trihydrate in 10 ml H_2O and add 280 ml methanol, 310 ml isopropanol and 180 ml toluene.

Mercaptan Analysis

Add 25 ml JP-5 to 100 ml of magic solvent and titrate with 0.002 M AgNO_3 .

3.5.2 Bomb Analysis

Samples were combusted in a Parr bomb according to ASTM D129-64, with sulfate assayed by ion chromatography (Dionex Corp.)

3.5.3 X-Ray Fluorescence

Samples were analyzed on a General Electric Model XRF-5 spectrometer according to ASTM 2622-77. The chromium x-ray tube was operated at 45 kV and 20 ma, using a helium tunnel, PET analyzing crystal, and a flow proportional counter run at 1400V. Counting time was 500 seconds.

4.0 MATERIALS COMPATABILITY INTRODUCTION

This task is motivated to resolve problems experienced by the Navy due to accelerated degradation of elastomeric seals in contact with JP-5 fuel. A major cause of such degradation has long been recognized to be excessive peroxide formation in hydrotreated fuels. Failure of a chloroprene diaphragm in A-7E aircraft was attributed to peroxide attack⁽⁹⁾. General Motors found that nitrile rubber reacted with peroxides in gasoline⁽¹⁰⁾.

NAVAIR conducted a survey of contractors to determine which elastomers are used in airframe fuel systems and how they behaved. The replies included the following:

- o Lockheed found nitriles gradually hardened...followed by cracking if highly stressed.
- o McDonnell had not tested nitriles to determine effects of peroxides, but did not recommend reuse of elastomers exposed to fuel and then air dried.
- o Rockwell used nitrile conforming to MIL-P-5315 and found that seals removed from service will exhibit cracks upon drying out.
- o Vought observed that nitrile O-rings from fuel systems must be replaced because of hardening, cracking and shrinking. Specifically, a commercial nitrile O-ring developed very deep cracks (1/3 of W dimension) after exposure to fuel containing 20 meq/l peroxide after 60 hours at 71°C (160°F).

From the breadth of types of nitrile rubber used in Navy systems, and the susceptibility of nitrile to peroxide attack, TRW conducted two parallel studies:

1. Increase our understanding of the relationship between peroxide and aromatic contents of JP-5 fuel, and degradation of nitrile elastomers, and

2. Identify or formulate elastomers compatible with JP-5 containing peroxides which could be used as alternatives to nitriles.

For the first approach, a standard nitrile compound was needed which could be used as a control throughout the program. Accordingly, Mr. Coleman Nadler of Naval Air Development Center was contacted for a recommendation. As a result of the conversation, it was decided to use a compound conforming to specification MIL-P-83461. This formulation was developed by Parker Seal Company under Air Force Contract in 1975. It is widely accepted as an improved nitrile and, in addition, its formulation is known. Service is directed toward MIL-H-5606 and MIL-H-83282 fluids, which are basically kerosene with chemical additives.

Control and experimental compounds for this program were compounded, molded, and tested in-house; thus, TRW was able to retain full knowledge of the rubber compositions. This type of information is usually proprietary to commercial manufacturers. In order to understand relationships between the JP-5 fuel containing peroxides and/or aromatics, it is first necessary to have a complete knowledge of the compounds under test.

Studies with nitrile rubber were divided into five areas under this program:

1. Identify an additive for existing nitrile rubber compounds that would protect the elastomer from peroxide attack. Following a search of chemical abstracts for chemicals that catalytically decompose peroxides and hydroperoxides, two were selected for evaluation - manganese dioxide and iron phthalocyanine. Details of this approach are presented in Section 5.1.

2. Understand the relationship between nitrile polymer backbone unsaturation and property retention of the nitrile compound. The primary site of nitrile degradation as a result of peroxide attack is probably a result of residual unsaturation ($>C=C<$) from the 1,4-butadiene content in the polymer backbone. A study was performed on nitrile:EPDM (EPDM is a saturated hydrocarbon) blends to understand the above relationship. This work is reported in Section 5.2

3. Study the effect of aromatic materials in JP-5 on property retention of nitrile rubber compounds as a function of nitrile polymer unsaturation. Conventional nitriles are copolymers of acrylonitrile (saturated backbone) and 1,4-butadiene (unsaturated backbone). As the acrylonitrile (ACN) content of the base polymer increases, the amount of polymer backbone unsaturation decreases. Four nitrile compounds ranging in ACN content from 27 to 50-mole% were tested in the presence of fuel "spiked" with three aromatics representative of those present in JP-5. Section 5.3 discusses this study.
4. Determine if changing from a peroxide-cure system for nitriles to a mixed sulfur/peroxide cure would provide a nitrile compound which is more resistant to peroxide attack. The study is presented in Section 5.4.
5. Evaluate the new highly-saturated nitrile polymers produced by Nippon Zeon Co., Ltd. as a direct substitute for conventional nitrile polymers currently used in Navy formulations. These polymers are reportedly manufactured by hydrogenating nitriles to produce a saturated backbone, and are therefore expected to overcome the weaknesses of conventional nitriles⁽¹¹⁾. Results of the evaluation are reported in Section 5.5.

As a corollary to the nitrile studies, rate of peroxide growth in JP-5 fuel independent of elastomer contact was determined for both virgin JP-5 fuel and JP-5 fuel saturated with manganese dioxide. Aging was conducted at four temperatures: 24°, 71°, 100°, and 135°C (75°, 160°, 212°, and 275°F, respectively). Section 5.6 presents this work.

There is little doubt that nitrile rubber is oxidized as a result of attack on the backbone carbon-carbon double bond. Of the alternative types of polymer which do not have backbone double bonds, fluorosilicones and phosphonitrilic (PNF) are reasonable candidates, but both are deficient in abrasion resistance and other strength properties.

Ethylene-propylene rubber swells excessively in hydrocarbons. Fluoro-elastomers generally have poor properties at low temperature. Other types of polymers such as epichlorohydrin, acrylics and siloxanes have additional problems for the intended service.

Two compounds were found which met the second objective of this task-to identify or formulate alternative elastomers that could be used in place of nitriles:

- o Firestone PNF-280-009
- o TRW Aflas/EPDM/chlorotrifluoroethylene (CTFE) terblend

Experiments conducted on the former are discussed in Section 5.7.

The latter compound was originally developed under Air Force Contract F33615-82-C-5041 for seals to be used in a high temperature/high pressure hydrocarbon fluid hydraulic system. The terblend also proved to be stable following exposure to JP-5 containing high levels of peroxides. Section 5.8 reports this work.

Optimization of the terblend involved compression set (Section 6.8.1), its excessive swell in JP-5 (Section 5.8.2), and extractability of the CTFE low temperature plasticizer by JP-5, as well as testing of possible alternative solvents as plasticizers (Section 5.8.3).

Conclusions and recommendations are listed in Sections 6.0 and 7.0, respectively.

5.0 MATERIALS COMPATABILITY TECHNICAL RESULTS

In keeping with the objectives of this task stated in Section 4.0, this section has been divided into studies with nitrile rubber (Sections 5.1-5.5) and alternative Polymer Systems (Section 5.6-5.8).

5.1 ADDITIVES FOR PEROXIDE-RESISTANT NITRILE RUBBER

It is clear both from the results of the NAVAIR survey discussed in Section 4.0 and a review of the literature, that peroxides cause degradation in nitrile elastomers. Work performed at General Motors and Goodyear also proved to be relevant to this program, some of which is presented below.

The General Motors research cited previously found that when nitrile rubber was stored in hydrocarbon fuel which started with 50 meq/l peroxide, the amount of peroxide slowly decreased and the nitrile degraded. This finding was consistent with work conducted previously at Goodyear⁽¹²⁾ and it was concluded that..."A rapid dropoff in PN [Peroxide Number] after exposure to elastomer indicated a reaction of the peroxide with the elastomer compound."

It is known that organic antioxidants added to nitrile rubber will provide an induction period before rubber degradation sets in. However, antioxidants are extractable, somewhat costly, and most interfere with the vulcanization of the rubber. Most types of antioxidants function by donating a hydrogen atom to terminate a free radical on the polymer. Therefore, the antioxidant is consumed in the process.

Extraction is countered by copolymerizing the antioxidant into the nitrile polymer⁽¹³⁾. However, other workers⁽¹⁴⁾ claim equivalent retention of properties after multiple oil-air aging cycles provided particular diamine antioxidants are added to the formulation. Consumption of hindered phenolic antioxidant is somewhat counteracted by the addition of certain regenerative thio compounds, notably dilaurythiodipropionate. This is also only a marginal improvement and Reference 15 concludes that "...the full potential of NBR [nitrile] is still far from being achieved."

With this background, TRW determined that a fresh approach was needed to protect nitrile rubber from oxidation. Because of the high ratio of fuel to

elastomer found in most fuel delivery systems, it was projected that a catalytic agent, rather than a stoichiometric agent, should be used.

Chemical Abstracts for 1979-1982 were searched for a list of chemicals that would decompose peroxides. These include:

<u>C. A. Reference</u>	<u>Peroxide Decomposer</u>
<u>87005142</u>	metal oxides
<u>91019539</u>	molybdenum oxide
<u>93238435</u>	vanadium or chromium oxides
<u>87133572</u>	transition metal salts
<u>86056117</u>	transition metal organic complexes
<u>92075573</u>	zeolite
<u>95008176</u>	dialkyl ester of thio tin
<u>96068151</u>	5-t-butyl-2-OH-phenyl sulfide
<u>89146201</u>	alkyl and aryl sulfides
<u>89031395</u>	sulfur-containing metal chelates
<u>97005657</u>	metal borides
<u>93149400</u>	zinc bis(0,0-dialkyl(aryl)-phosphorodithionate)
<u>91074176</u>	palladium II
<u>8610561</u>	platinum
<u>91210657</u>	metal acetylacetonates
<u>96019443</u>	nickel bis(acetylacetonate)
<u>94102649</u>	iron and cobalt phthalocyanine

The list was refined by deleting dangerous and costly chemicals. Two of the remaining chemicals were then selected for evaluation. Manganese dioxide (MnO_2) and iron phthalocyanine were mixed with JP-5 and aged without rubber at 100°C (212°F). The manganese dioxide sample remained clear and mobile while the phthalocyanine and control samples of fluid became dark and more viscous after three days. This result led to the decision to continue the study with adding the chemicals separately to the rubber.

Iron phthalocyanine and MnO_2 were added to the MIL-P-83461 compound in different ways. MnO_2 was added prior to vulcanization and iron phthalocyanine was added by swelling the vulcanized rubber with an acetone suspension of the

chemical and allowing the acetone to evaporate. Table 11 reports the compositions. Compound 14310-15-1 of the table conforms to MIL-P-83461, and as suggested by Coleman Nadler of NADC, is used as the control nitrile compound throughout this task.

Table 11. Compositions of Nitrile Rubber Compounds

<u>Component/Compound</u>	<u>14310-15-1</u> <u>MIL-P-83461</u>	<u>14310-15-2</u>	<u>14310-15-3</u>
Krynac 27.50	95	95	95
SBR 1500	5	5	5
Magnesium Oxide	5	5	5
Cadmium Oxide	4	4	4
FEF Carbon	30	30	30
SRF Carbon	30	30	30
MT Carbon	30	30	30
DL-2 Ethyl Hexyl Azelate	5	5	5
Dibutoxyethyl Sebacate	5	5	5
Aminox Antioxidant	1	1	1
Zenite Antioxidant	1	1	1
Lupersol 101 Peroxide	1.5	1.5	1.5
Manganese Dioxide	--	--	2.1
Iron Phthalocyanine	--	2.0	--
Cure: 5'/188°C (370°F)	212.5	214.5	214.6

Samples of the above materials were aged in JP-5 (fluid sample number NFP-2) and in JP-5 doped with 1% w/w MnO₂. Aging temperatures were 70°C (158°F) and 100°C (212°F) for 72 hours. The samples of rubber were removed and allowed to air dry for three days prior to testing. It is important to note that there were four containers aged at each temperature. They are identified as follows:

<u>Container</u>	<u>Identification</u>	<u>Fluid Composition</u>	<u>Contained (see Table 11)</u>
1	Fluid A	JP-5	Control, Sample 15-3
2	Fluid B	JP-5 plus 1%w/w MnO ₂	Control, Sample 15-3
3	Fluid A	JP-5	Sample 15-2
4	Fluid B	JP-5 plus 1%w/w MnO ₂	Sample 15-2

Rubber containing phthalocyanine was aged separately from the other rubber as there was phthalocyanine on the surface of the sample which could contaminate the fluid.

Post-test samples of the fluid were analyzed for peroxide content in accordance with ASTM D3703-78 with the following exception: prior to contacting with aqueous potassium iodide, the fuel was dissolved in Freon TF instead of carbon tetrachloride. Peroxides are reduced by the potassium iodide liberating an equivalent amount of iodide that is titrated with sodium thiosulfate solution. All four fluids aged at 70°C (159°F) showed little or no peroxide buildup as indicated in Table 12. Two very different results were found for the fluids aged at 100°C (212°F). Fluids containing phthalocyanine generated considerable peroxide. Given that iron phthalocyanine has a structure much like hemoglobin, it is theorized that the chemical solubilizes oxygen and enhances peroxide production more effectively than it catalyzes the decomposition of peroxides.

Table 12. Peroxide Contents of Aged JP-5 Fluid^{a)}

<u>Fluid Sample^{b)}</u>	<u>Storage Temperature, °C</u>	<u>Peroxide, meq/L</u>
Container 1	70°	0.2
Container 2	70°	0.0
Container 3	70°	1.1
Container 4	70°	0.3
Container 1	100°	0.8
Container 2	100°	0.8
Container 3	100°	35.1
Container 4	100°	99.6

a) Original fluid contained nil peroxide.

b) See previous Table for composition

The data in Table 13 show that MnO_2 had a very minor effect on the vulcanization process, whereas phthalocyanine was added after the vulcanization process and therefore had no effect on the properties.

At 70°C (159°F) clear differences are being developed between the samples. First, the control has only minor degradation, in contrast to what was expected. The MnO_2 sample, it is important to note, was in the same container of fluid as the control and it is possible that MnO_2 diffused into the fluid. Recall from Table 12 that there was essentially no peroxide (<1 meq/l) in the JP-5 fluid in this container. Thus, we interpreted this result to mean that MnO_2 in very low concentration could possibly prevent formation of, or decompose, peroxides in JP-5.

The rubber containing iron phthalocyanine was thoroughly degraded. As stated in Table 12 these samples were in a separate container, one that had 99.6 Meq/l of peroxide at the end of the test. In our tests, the peroxide level grew from near 0 to 99.6 Meq/l while the rubber in the same container was being degraded. Given that rubber degradation consumes peroxide in the usual test (References 10 and 12), the production of peroxides in the presence of iron phthalocyanine must be very rapid indeed.

In order to determine if our observations on the stability of fuel with added MnO_2 were based on the solution of MnO_2 in the fuel, samples of JP-5 were prepared in which 1% w/w of MnO_2 was added and the mixture stirred. Most of the MnO_2 settled to the bottom of the container. An analysis of the fuel sample determined that approximately 2 ppm of MnO_2 is soluble at ambient temperature.

Using this fluid, samples of rubber were again stored for 72 hours at 70°C (159°F) and 100°C (212°F) and then air dried three days at ambient conditions.

Table 14 reports the data from this experiment.

As before, JP-5 exposed to MnO_2 in the absence of phthalocyanine, did not degrade the nitrile rubber. Comparing the properties in Table 13 with the corresponding properties in Table 14 indicates there is essentially no difference in degradation between the nitrile compounds aged in virgin JP-5 and those aged in JP-5 doped with MnO_2 . However, since the control nitrile and the nitrile containing MnO_2 were aged in the same container, it was

The rubber samples were analyzed for mechanical property retention. Nitrile oxidatively ages by crosslinking, consistent with the cracking and brittleness reports of the airframe contractors described previously. Thus, moduli and hardness tend to increase, elongation at break tends to decrease.

ASTM D412 was used to determine stress-strain properties and Shore A hardness was measured by ASTM D2240. Table 13 reports the data from the samples. The area under the stress strain curve is used in comparing elastomers as a measure of toughness. It is estimated by multiplying tensile strength by elongation and dividing by two to reflect the approximate right triangle shape of the stress vs strain curve.

Table 13. Properties of Nitrile Rubber Compounds Following Aging 72 Hrs. in JP-5 and 72 Hrs. in Ambient Air

Sample 14310-	Property	Virgin	JP-5/70°C	JP-5/100°C
15-1: MIL-P-83461 (Control)	M ₁₀₀ , psi ^{a)}	435	620	421
	M ₂₀₀ , psi	1305	1945	1368
	T _B , psi ^{b)}	2055	2185	1895
	E _B , % ^{c)}	285	215	255
	Shore A ^{d)}	70	73	70
	Area X10 ⁻³	392	231	242
	% Area Detained	-	79	82
15-2: With Phthalo- Cyanine	M ₁₀₀ , psi	435	700	-
	M ₂₀₀ , psi	1305	2030	-
	T _B , psi	2055	2095	315
	E _B , %	285	210	50
	Shore A	70	75	70
	Area X10 ⁻³	293	220	8
	% Area Retained	-	75	3
15-3: With MnO ₂	M ₁₀₀ , psi	525	610	620
	M ₂₀₀ , psi	1525	1915	1825
	T _B , psi	2005	2175	1985
	E _B , %	245	220	215
	Shore A	71	73	73
	Area X10 ⁻³	246	239	213
	% Area Retained	-	97	86

a) Modulus at 100% elongation.

b) Ultimate tensile strength.

c) Ultimate elongation.

d) Shore hardness.

Table 14. Properties of Nitrile Rubber Compounds Following Aging 72 Hours in JP-5 Doped With MnO_2 and 72 Hours in Ambient Air

Sample 14310-	Property	Virgin	Doped JP-5/70°C	Doped JP-5/100°C
15-1: MIL-P-83461 (Control)	M_{100} , psi	435	675	440
	M_{200} , psi	1305	1900	1315
	T_B , psi	2055	2070	1865
	E_B , %	285	200	255
	Shore A	70	73	70
	Area $\times 10^{-3}$	293	207	238
	% Area Retained	-	71	81
15-2: With Phthalocyanine	M_{100} , psi	435	590	-
	M_{200} , psi	1305	1850	-
	T_B , psi	2055	1080	230
	E_B , psi	285	220	20
	Shore A	70	75	74
	Area $\times 10^{-3}$	293	229	2
	% Area Retained	-	78	1
15-3: With MnO_2	M_{100} , psi	525	625	480
	M_{200} , psi	1525	1900	1545
	T_B , psi	2005	2240	1865
	E_B , %	245	225	230
	Shore A	71	73	70
	Area $\times 10^{-3}$	246	252	214
	% Area Retained	-	102	87

unclear whether the similar degradation in the two nitriles occurred because the MnO_2 diffused out of one and reduced the peroxides in the fuel, or because MnO_2 was not an effective catalytic agent as a peroxide decomposer. In addition, the post-test peroxide levels of the fuels were in all cases equal to or less than 0.8 ppm (initially level equaled zero); thus, there may not have been enough peroxide to show significant differences in degradation in the three day aging period.

A further set of experiments was therefore conducted to determine if MnO_2 additive will succeed in protecting nitrile rubber under conditions such that massive peroxide attack is expected, and no compromise of the results, as described above could occur.

The MIL-P-83461 nitrile and the nitrile containing MnO_2 were re-made as compounds 14310-21-1 and 21-2, respectively according to the formulations listed for compounds 14310-15-1 and 15-3 in Table 11. Samples of the two compounds were immersed in separate containers of JP-5 fuel (NFP-2) containing significant levels of peroxide [18.3 meq/l (146 ppm)].

The peroxide was "grown" in the fuel by aging JP-5 16 hr/100°C (212°F) followed by a seven day exposure to ambient air.

Tensile bars of each compound were individually aged in test tubes containing JP-5 under the following conditions to accelerate aging effects and to determine the effect of adding MnO_2 to nitrile:

- o 72 hr/100°C (212°F) 72 hr/RT
- o 1 wk/135°C (275°F)

The latter temperature was selected following information from Navy sources indicating the temperature range of Navy fuel is -44 to 150°C (-47 to 300°F). Table 15 reports the data from these experiments. As indicated by the data, similar degradation was observed in the two compounds, leading to the conclusion that MnO_2 is not an adequate additive to nitrile to reduce peroxide attack.

Since earlier experiments had lead to the postulate that oxidative attack and peroxide attack occur by separate mechanisms and at different rates, TRW next conducted an experiment designed to distinguish these two modes of attack. Our premise was that a fuel sample with MnO_2 added will transport oxygen but not form peroxides, while a peroxide-containing fuel, sparged with

Table 15. Properties of Peroxide-Cured Nitrile Compounds Following Aging

Compound 14310-21-1 (MIL-P-83461)				Compound 14310-21-2 (MIL-P-83461 + MnO ₂)		
Property	Virgin	After 72 hr/100°C +72 hr/RT	After 1 wk/ 135°C	Virgin	After 72 hr/100°C +72 hr/RT	After 1 wk/ 135°C
M ₁₀₀ , psi	324	314	508	354	341	546
M ₂₀₀ , psi	1038	1018	--	1134	1094	--
T _B , psi	1892	1318	655	1897	1238	546
E _B , %	315	235	115	295	220	100
Shore A	70	65	60	69	65	64
S/S Area x 10 ⁻³	298	155	38	280	136	27
% Area Retained	--	52	13	--	49	10
Peroxide in Post Test Fuel* [meq/l (ppm)]	--	7.1 (57)	3.5 (28)	--	7.2 (58)	3.5 (28)

*Initial level= 18.3 meq/l (146 ppm)

argon will furnish peroxide but not oxygen. The nitrile rubber was tested in these two different fuels over a range of temperatures and times.

For this study a sulfur cured nitrile compound containing no additional antioxidants (a small amount of antioxidant is present in the polymer) was selected from Reference 15. Table 16 reports the exact formulation. Three temperatures were selected for aging for three weeks each: RT, 70°C (159°F) and 100°C (212°F). Two fuel samples were prepared as follows for each temperature:

"A" Fluid - JP-5 (0 ppm peroxide) with 1% w/w MnO_2 in bottom of flask, exposed to air for analysis of oxidative attack.

"B" Fluid - JP-5 (292 ppm peroxide) sparged and blanketed with argon for analysis of peroxide attack.

Thus, the test matrix was as follows:

<u>3 Weeks/°C</u>	<u>JP-5/MnO_2/Air</u>	<u>JP-5 (292 ppm)/Argon</u>
RT	X	X
70°C (158°F)	X	X
100°C (212°F)	X	X

Table 16. Composition of Sulfur Cured Nitrile Compound (14310-38)

<u>Component</u>	<u>Parts by Weight</u>
Chemigum N917	100
Zinc Oxide	5
Stearic Acid	1
SRF Carbon	75
Di Octyl Sebacate	20
Sulfur	1.5
MBTS Accelerator	1.5
Monex Accelerator	<u>0.4</u>

Cure: 20'/152°C (307°F)

Three tensile specimens were individually aged in test tubes per the matrix (18 total samples). Following aging for three weeks, the samples were dried at ambient temperature for 24 hours under vacuum. Post-test fluids were analyzed for peroxide content. The resultant data are listed in Table 17.

Figure 16 plots the stress-strain areas listed in Table 17 as a function of aging temperature. The properties of the samples aged in the "A" fluid are essentially identical (within experimental error) to those of the samples aged in the "B" fluid at RT and 70°C (158°F). Only at 100°C (212°F) does the sample exposed to the high amount of peroxide show higher degradation than the one exposed to the fluid which had an initial peroxide concentration of 0 ppm.

Thus, it appears as if both sets of samples exhibited peroxide attack. In the "A" fluid, although initially there was no peroxide, any peroxide grown was consumed by the rubber. In the "B" fluid, where a high amount of peroxide was initially present, as the temperature increased, the rate of peroxide consumption by the rubber (and thus, attack of the rubber leading to degradation of properties) increased, resulting in low peroxide amounts in the post-test fuels. This is probably why the two curves in Figure 16 are almost superimposed.

Attention was next directed at determining if MnO_2 could reduce peroxides when added directly to the fuel in small amounts. For this experiment four samples were aged 2 wks/70°C (159°F):

<u>Fuel</u>	<u>Initial Peroxide (ppm)</u>
1) JP-5	0
2) JP-5 + 1% w/w MnO_2	0
3) JP-5 with "grown" peroxides	292
4) JP-5 with "grown peroxides + 1% w/w MnO_2	292

(The above peroxide was "grown" in the latter two samples by aging the fuel 72 hr/135°C (275°F) followed by 72 hr/RT). It was previously determined that MnO_2 is soluble in JP-5 at ambient temperatures in the order of 2 ppm. An excess was used in this experiment to study effects of MnO_2 addition to the fuel. No elastomer samples were present. Following aging, the peroxide levels were as follows

Table 17. Properties of Sulfur-Cured Nitrile Compound After Three-Week Aging

<u>Before Aging</u>			
	M ₁₀₀ , psi	384	
	M ₂₀₀ , psi	1096	
	T _B , psi	1589	
	E _B , %	260	
	Shore A	67	
	Area x 10 ⁻³ *	207	
Temp	Properties	"A" fluid 0 ppm JP-5 + MnO ₂ /air	"B" fluid 292 ppm JP-5/Argon
RT	M ₁₀₀ , psi	375	381
	M ₂₀₀ , psi	1048	1034
	T _B , psi	1812	1883
	E _B , %	280	305
	Shore A	70	70
	Area x 10 ⁻³	254	286
	Post-test peroxide (ppm)	0	81.2
70°C	M ₁₀₀ , psi	419	444
	M ₂₀₀ , psi	--	1400
	T _B , psi	1346	1400
	E _B , %	190	200
	Shore A	70	67
	Area x 10 ⁻³	128	140
	Post-test peroxide (ppm)	0	11.8
100°C	M ₁₀₀ , psi	489	695
	M ₂₀₀ , psi	--	--
	T _B , psi	1468	1186
	E _B , %	165	140
	Shore A	70	70
	Area x 10 ⁻³	121	83
	Post-test peroxide (ppm)	6.8	13.5

*An estimate of total work to failure calculated by $1/2 E_B \times T_B$

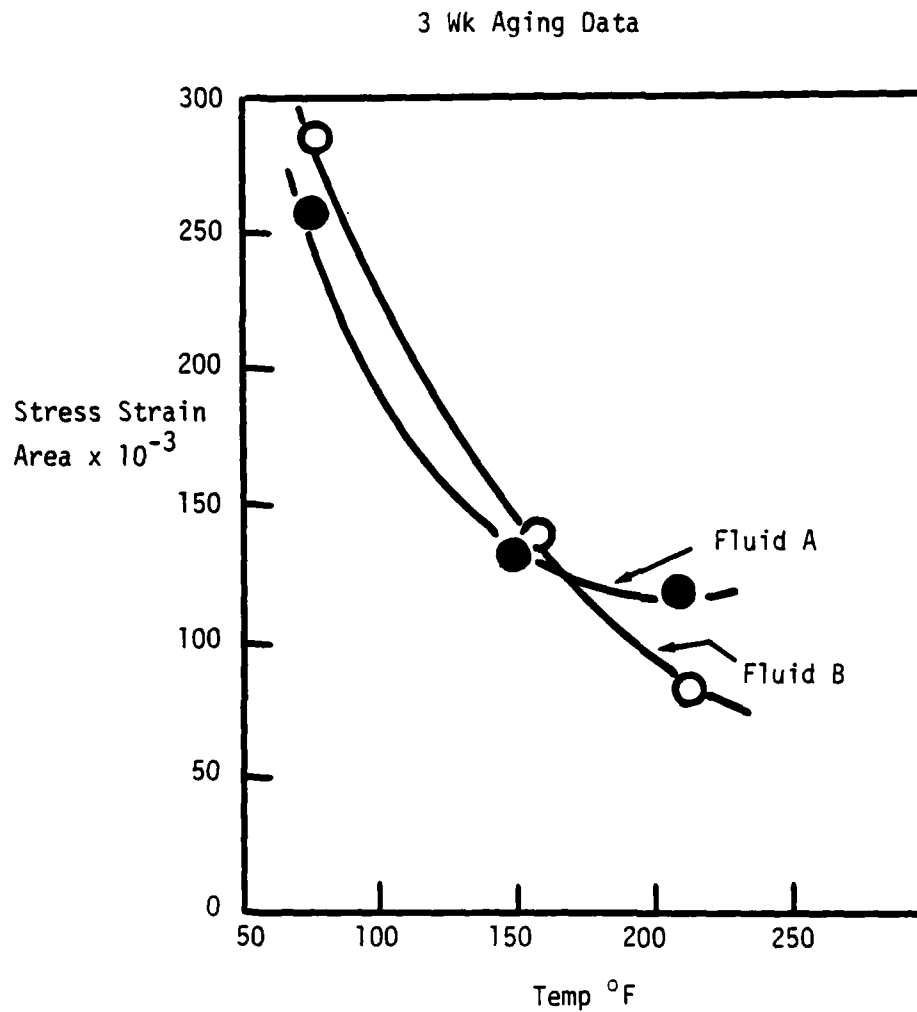


Figure 16. Stress-Strain Areas as a Function of Aging Temperature for Nitrile Rubber in Fluid A and Fluid B (Favoring Oxygen Attack and Peroxide Attack, Respectively).

<u>Sample</u>	<u>Post-Test Peroxide (ppm)</u>
1	686
2	943
3	965
4	814

Following review by the Navy of the above MnO_2 studies, a consensus was reached that the concentrations of peroxide [>12.5 meq/l (100 ppm)] fuel used to determine possible advantages of MnO_2 were too high. An experiment was therefore conducted with JP-5 fuel with an initial peroxide concentration of 1.4 meq/l (11.3 ppm).

The two formulations used previously -- MIL-P-83461 and MIL-P-83461 with 1% w/w MnO_2 -- were again evaluated (see Table 18 for formulations). Samples of the two compounds were individually aged in test tubes containing JP-5 (NFP-2) at 71°C (160°F) for one, two, four, and eight weeks. JP-5 samples containing no elastomers were concurrently aged to determine the level of peroxides generated in the fuel under these conditions.

Following removal at the appropriate aging periods, samples were dried 16 hr/80°C (176°F) in vacuo to remove residual fuel before measuring tensile properties. Table 18 compares the results of the two compounds.

Tensile properties of the compound containing MnO_2 were in general lower than those of the MIL-P-83461 control, while elongation at break tended to be higher, indicating a slightly lower state of cure. Thus, the percent area under the stress-strain curve retained is listed to compare the samples on a one-to-one basis. These values are plotted in Figure 17. The curves drawn were fitted by computer using a regression analysis. The equations for the curves are as follows, where t equals time aged in weeks:

MIL-P-83461 Compound:

$$\text{Area Retained (\%)} = 96.33 - 0.22t - 0.19t^2 \quad R^2 = 0.59$$

MIL-P-83461 + 1% MnO_2 :

$$\text{Area Retained (\%)} = 69.50 + 20.42t - 2.69t^2 \quad R^2 = 1.00$$

Table 18. Evaluation of MnO₂ Additive in MIL-P-83461 Compound

Aging Period Weeks	MIL-P-83461 (Sample 14310-90-1)							MIL-P-83461 + 1% W/W MnO ₂ (Sample 14310-90-2)							Peroxide in JP-5 Fuel Alone (ppm)
	M ₁₀₀ psi	T _B psi	E _B %	Shore A	Area Retained %	Peroxide in Post-Test Fuel meg/l	Peroxide in Fuel (ppm)	M ₁₀₀ psi	T _B psi	E _B %	Shore A	Area Retained %	Peroxide in Post-Test Fuel meg/l	Peroxide in Fuel (ppm)	
0	3259	4543	120	83	—	—	—	2667	4282	145	83	—	—	—	1.4 (11.3)
1	4000	4737	115	88	100	0.13	(1.0)	3789	4693	115	88	87	0.11	(0.9)	5.5 (44.0)
2	3973	4557	105	88	88	0.13	(1.0)	2732	4300	145	85	100	0.13	(1.0)	14.0 (112.0)
4	4176	4759	110	88	96	0.19	(1.5)	3613	5161	130	85	108	0.15	(1.2)	85.1 (681.0)
8	3747	4051	110	87	82	0	(0)	3360	3443	110	85	61	0	(0)	21.6 (173.0)

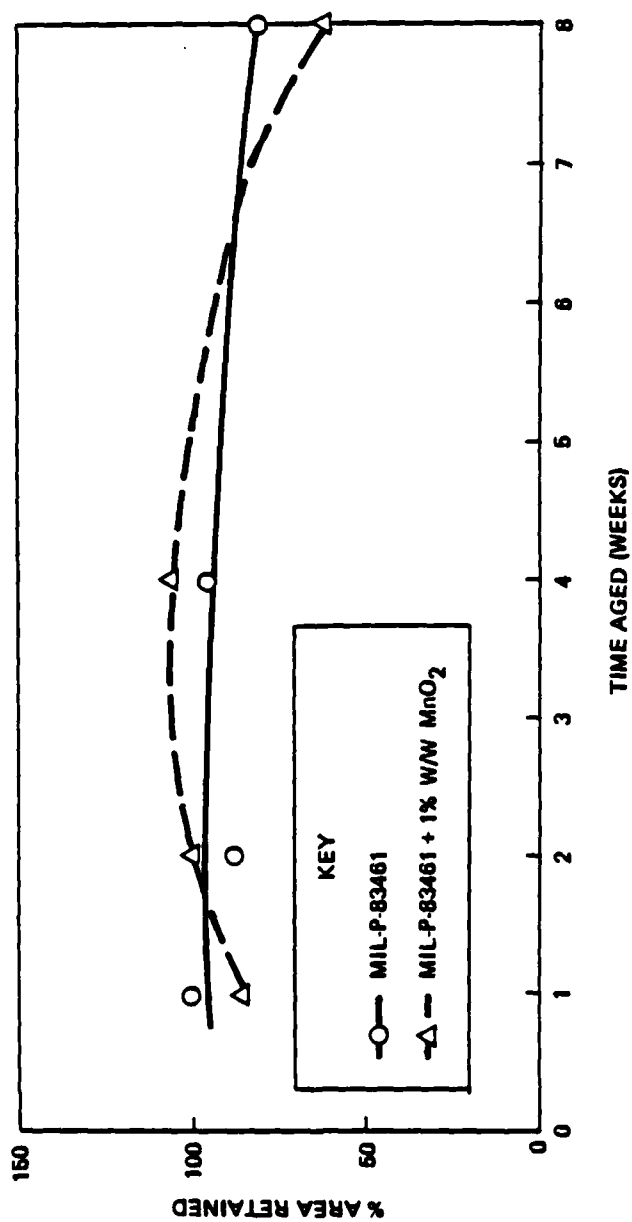


Figure 17. Effect of Aging in JP-5 on Property Retention of MIL-P-83461 Compounds

R^2 is the correlation coefficient which indicates how well the data fit the equations. A value of unity indicates a perfect fit. Although R^2 for the first equation was 0.59, the curve was relatively flat, which greatly influenced the correlation coefficient. As can be seen in Figure 17, the data fit the curve shown fairly well.

Thus, it is concluded that MnO_2 is not effective for peroxide decomposition either added to the rubber or the fuel. The fuels that were aged previously in the presence of elastomers apparently resulted in low post-test concentrations of peroxide because the peroxide was being consumed by the rubber as fast as it could be generated. Once all available sites in the rubber compound are attacked--leading to degradation of properties--peroxide concentration in the fuel increases.

5.2 PROPERTY RETENTION OF NITRILES AS A FUNCTION OF UNSATURATION

The primary site of nitrile rubber degradation as a result of peroxide attack is probably in residual unsaturation ($>C = C<$) from the 1,4-butadiene content in the polymer backbone. A study was performed on nitrile:EPDM polymer blends to understand the relationship between backbone unsaturation and tensile property retention.

Nitrile rubber is copolymerized from butadiene and acrylonitrile (ACN). EPDM is a completely saturated hydrocarbon polymer, and thus, degradation is expected to occur within the non-EPDM component of the blends (i.e., EPDM is a chemically inert diluent for nitrile rubber under the test conditions). Figure 18 depicts the polymer structures used for this experiment.

Six acrylonitrile:EPDM blends were formulated. Five used Polysar's Krynac 38.50 (38 percent w/w acrylonitrile and about 60 percent 1,4-butadiene), and varied in nitrile:EPDM blend ratio between 100:0 and 75:25. One 85:15 blend was also made using Goodyear's Chemigum N917 (22 percent w/w acrylonitrile and about 70 percent 1,4-butadiene), to directly compare the effects of a higher butadiene content. Table 19 lists the formulations considered.

Samples were aged 1 week/135°C (275°F) in JP-5 containing about 3.8 meq/l (30 ppm) peroxide. Swell properties at 135°C were determined on both molded O-rings and tensile specimens cut from a molded slab. Compression set

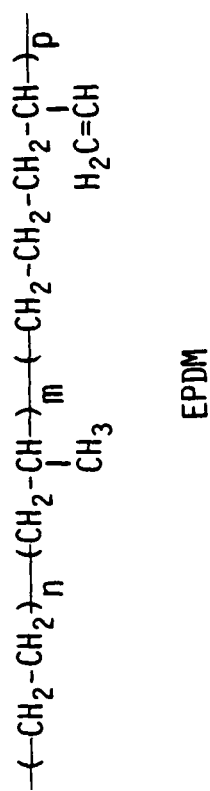
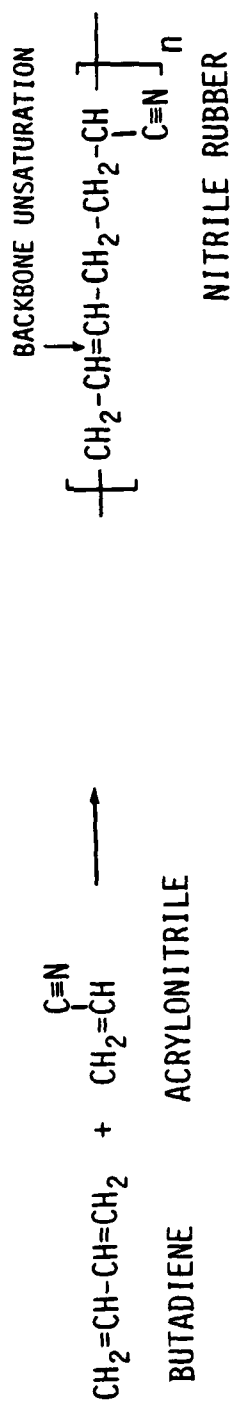


Figure 18. Polymer Structures for Nitrile: EPDM Study

Table 19. Formulations of Nitrile:EPDM Blends

<u>Component</u>	<u>Master- batch A</u>	<u>Master- batch B</u>	<u>Master- batch C</u>			
Krynac 38.50	100	-	-			
Chemigum N917	-	-	100			
Nordel 1040	-	100	-			
MT Carbon	75	-	75			
Antioxidant 2246	2	-	2			
Teflon T-8A	3	15	3			
Zinc Oxide	5	5	5			
Cab-O-Sil M5	-	25	-			
Vinyl Silane A-172	0	1	-			
Agerite Resin D	0	0.5	-			
B-3000 Resin	0	25	-			
Sulfur	0.3	-	0.3			
DiCup R Peroxide	4.9	2.1	4.9			
<u>Blend Formulations¹</u>						
Compound 14310-69	-1	-2	-3	-4	-5	-6
% Krynac 38.50	100	95	90	85	75	-
% Nordel 1040	-	5	10	15	25	15
% Chemigum N917	-	-	-	-	-	85

¹Values listed are on a polymer:polymer basis; i.e., Compound 69-2 is 95% w/w polymer in Masterbatch A:5% w/w polymer in Masterbatch B.

following 72 hours/135°C and TR_{10} values were determined only for virgin samples, as the hardness of the aged samples precluded testing.

Tensile properties were determined per ASTM D412. all resultant physical properties are listed in Table 20. The post-test fuel was analyzed for peroxide contents; the results are also included in Table 20.

Table 21 lists the percent unsaturation ($>C = C<$) for each blend and the respective percent areas retained. These values are also plotted in Figure 19. (Appendix C shows a sample calculation of backbone unsaturation.)

A linear regression analysis was determined by computer to give the equation that best fit the data of the Krynac:EPDM blends. The point corresponding to Compound 69-4 (10.7 percent $>C = C<$) was omitted from the analysis, as some of the fuel in this sample evaporated during aging, leaving the sample partially exposed to air. The equation determined by computer relating property retention to backbone unsaturation is:

$$\% \text{ Area Retained} = -2.99 \times \%(C=C) + 45.7 \quad (\text{Correlation Coeff., } R^2 = 0.98)$$

indicating every one percent increase in backbone unsaturation causes a three percent loss in property retention.

The above equation suggests the Navy can improve performance of nitrile seals by using polymers with high acrylonitrile contents. (Results of a study reported in Section 5.3 shows a nitrile with an ACN content of 40 mole-% is optimum).

5.3 EFFECT OF AROMATICS IN FUEL ON NITRILE DEGRADATION

In addition to studying the effect of peroxides on nitrile degradation, the Navy also desired to know the effect of aromatics in JP-5 on the stability of nitrile compounds. TRW elected to test along with our conventional control compound (conforming to MIL-P-83461 using Krynac 27.50 as the base polymer), three other Krynac polymers with higher acrylonitrile (ACN) contents.

Krynac^R elastomers are representative of nitriles used by industry, which have 90% of their unsaturation in the polymer backbone. As outlined in Table 5 of the previous section, nitrile compounds consist of an acrylonitrile

Table 20. Physical Properties of Nitrile:EPDM Blends¹

-1 (100% A) Virgin	(psi)	(psi)	(psi)	153	Shore	O-rings	D1729	Compression ³	-27.5	Peroxide
<u>Compound</u> <u>14310-69</u>	<u>M₁₀₀</u> <u>(psi)</u>	<u>M₂₀₀</u> <u>(psi)</u>	<u>T_B</u> <u>(psi)</u>	<u>E_B</u> <u>(%)</u>	<u>Shore</u> <u>A</u>	<u>ΔV%</u> <u>2-214</u> <u>O-rings</u>	<u>ΔV%</u> <u>D1729</u> <u>a/c</u>	<u>Compression³</u> <u>Set</u> <u>(%)</u>	<u>TR₁₀</u> <u>(C)</u>	<u>Peroxide</u> <u>Posttest</u> <u>ppm</u>
-1 (100% A) Virgin	970	-	1734	185	78	4.4	10.5	25.7	-27.5	7
Aged ²	-	-	884	30	89	-	-	-	-	-
-2 95% A: Virgin	974	1693	1815	230	74	6.1	14.4	33.3	-28	4
5% B Aged	-	-	964	45	87	-	-	-	-	-
-3 90% A: Virgin	932	1642	1747	235	77	7.7	18.5	39.4	-28	3
10% B Aged	-	-	987	55	88	-	-	-	-	-
-4 85% A: Virgin	1021	1558	1684	240	82	7.7	37.6	31.4	-25.5	4
15% B Aged ⁴	-	-	958	30	87	-	-	-	-	-
-5 75% A: Virgin	1077	1460	1646	250	84	8.9	41.0	48.5	-29.5	3
25% B Aged	-	-	1154	60	90	-	-	-	-	-
-6 85% C: Virgin	927	988	1709	150	82	7.3	19.9	25.7	-44	2
15% B Aged	-	-	800	40	84	-	-	-	-	-

¹A = Krynac 38.50; B = EPDM, C = Chemigum N917; see Table 2.1 for details.

²Aged 1 week/275°F (135°C) in JP-5 (30 ppm peroxide); dried 16 hours/212°F (100°C) in vacuo.

³Following 72 hours/275°F (135°C) per ASTM D395 Method B.

⁴Some fuel evaporated, leaving sample partially exposed to air.

Table 21. Property Retention of Nitrile:EPDM Blends

<u>Compound</u> <u>14310-69</u>	<u>% C = C in Backbone</u>	<u>Area x 10⁻³</u> <u>Virgin</u>	<u>Area x 10⁻³</u> <u>Aged</u>	<u>% Area</u> <u>Retained</u>
-1	12.3	160	13	8.1
-2	11.8	209	22	10.5
-3	11.2	205	27	13.2
-4	10.7	202	14	7.1
-5	9.5	206	35	16.8
-6	12.1	128	16	12.5

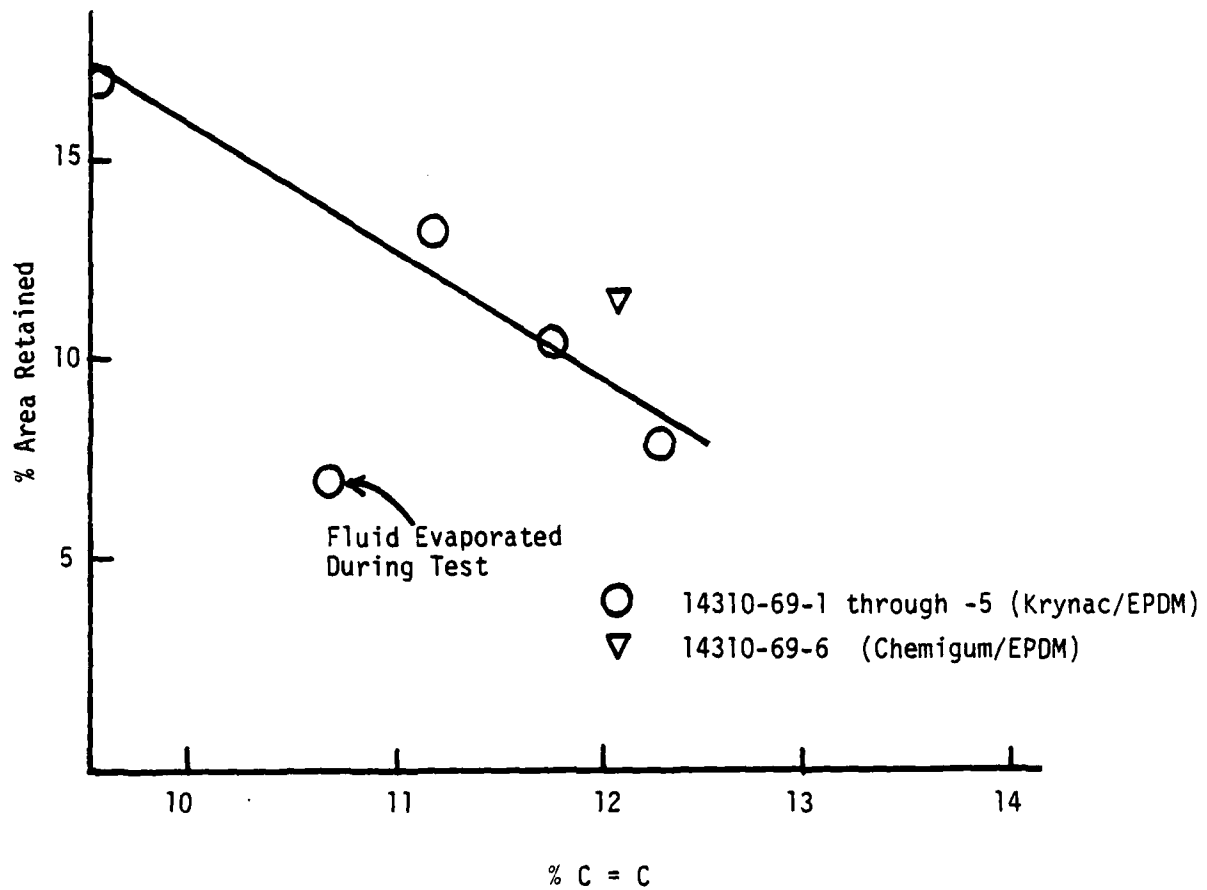
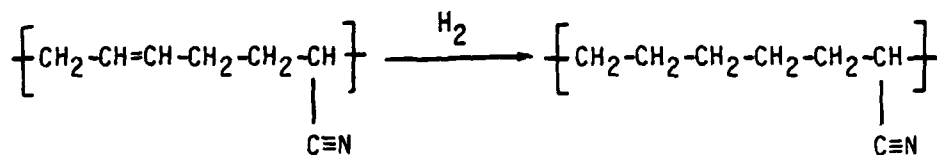


Figure 19. Area Retained in Nitrile: EPDM Blends versus Carbon Unsaturation. $\% \text{ Area Retained} = 2.99 (\% \text{ C}=\text{C}) + 457$. Correlation Coefficient = 0.977

component and an unsaturated butadiene component. As the acrylonitrile content is increased, the amount of unsaturation is decreased. In this manner, the effects of aromatics on nitrile property retention, as a function of polymer unsaturation, was determined.

Four nitrile compounds ranging in ACN content from 27 mole-% to 50 mole-% were prepared according to the formulations in Table 12. Also added to the study was a cured slab of National O-ring Company's Compound 89D8, which is made from Nippon Zeon's highly saturated nitrile (HSN). As reported in Reference 11 HSN is made by hydrogenating nitriles to produce a saturated backbone, and are therefore expected to overcome the weaknesses of conventional nitriles:



CONVENTIONAL NITRILE

HSN

(The evaluation of HSN is further explored in Section 5.5)

Compound 89D8 was included in the aromatic study to determine if the new nitrile is more stable to aromatics. Because the National O-Ring formulation is proprietary, it was not possible to make a direct comparison with the other samples.

The fuel used for the aromatic study was N1010-250 Thinner manufactured by the Oil and Solvent Process Company (OSCO) of Azusa, California. N1010-250 thinner contains 38.8% naphthenes, 60.0% paraffins, and 1.2% aromatics, and has a boiling range of 206-252°C (403°-486°F). It was selected as a substitute for JP-5, as the latter contains 10% aromatics which cannot be easily removed, preventing the establishment of a baseline.

Three aromatics shown in Table 23 were selected as being representative of those present in JP-5 (structures are shown in Appendix D):

Table 23. Selected Aromatics

	<u>b.p. °C (°F)</u>
o mesitylene (1,3,5-trimethylbenzene)	163-166 (325-331)
o durene (1,2,4,5-tetramethylbenzene)	205-205 (399-401)
o dimethylnaphthalenes	262-269 (504-516)

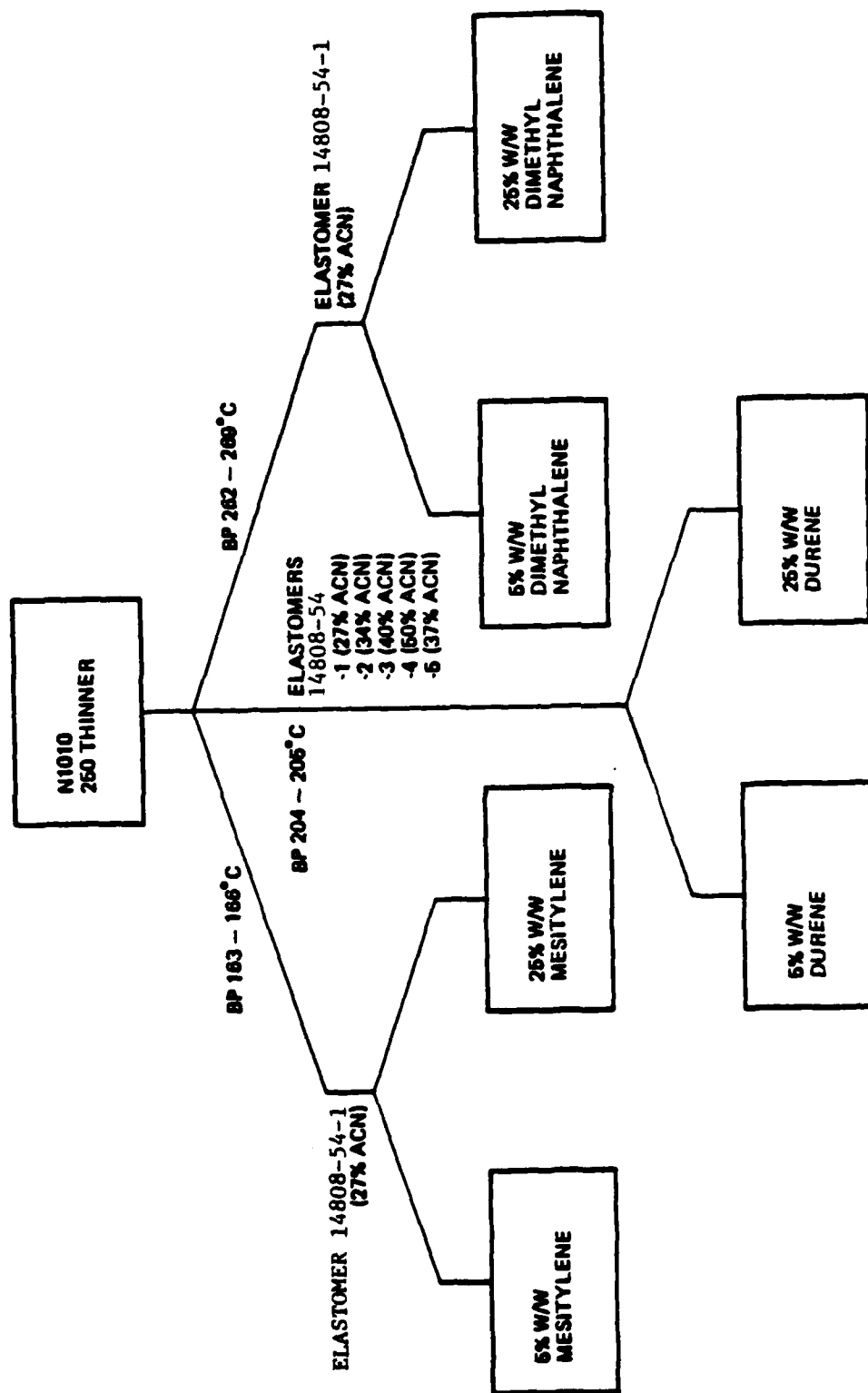
The N1010-250 thinner was spiked at a low (5% w/w) and high (25% w/w) level with each aromatic compound, consistent with the specification limits for JP-5.

Figure 20 outlines the experimental plan for determining the effects of aromatics on the properties of the nitrile compounds listed in Table 22. The four Krynac compounds were aged one, two, four, six, and eight weeks at 71°C (160°F). The HSN Zetpol compound was only aged one and two weeks because of limited material, and length of time remaining to conduct the experiment after the sample was received.

Three tensile bars per aging period were individually aged in test tubes containing the appropriate aromatic fuel. Samples were also aged for each time period in N1010-250 thinner (neat fuel) as controls to separate the effects of the aromatics from the effect of the thinner. Following each aging period, the tensile bars were dried for 16 hr at 30°C (86°F) in vacuo to remove all solvent residue prior to determining tensile properties.

Tables 24, 25, and 26 list the resultant properties which are graphically depicted in Figures 21 through 29. Table 24 lists the properties of the controls as a function of time. Retention of the area under the stress-strain curve (estimated by 1/2 tensile strength x elongation at break) was used as a measure of degradation. Table 25 lists the properties of the MIL-P-83461 control compound (Krynac 27.50) aged in all fluids; Table 26 lists the properties of all other compounds aged in durene.

Figures 21, 22, and 23 show the effects of aging the MIL-P-83461 control compound (Krynac 27.50 base nitrile) in mesitylene, dimethylnaphthalenes, and durene, respectively. In each graph, no apparent effect is seen by increasing the aromatic concentration from 5 to 25%. In addition, the compound's ability to retain its properties appears improved by the addition of the aromatics.



COMPOUNDS 14808-54-1 THROUGH -4 TO BE AGED 71°C (160°F) FOR 1, 2, 4, 6 AND 8 WEEKS;
 COMPOUND 14808-54-5 TO BE AGED FOR 2 AND 4 WEEKS ONLY DUE TO LIMITED SAMPLE AND TIME.

Figure 20. Summary of Experimental Plan to Determine Effect of Aromatics on Properties of Nitrile Compounds

Table 22. Nitrile Compounds for Aromatic Study

Formulation Conforming to MIL-P-83461 with Base Polymer Variation*

	<u>Parts by Weight</u>
Nitrile Polymer**	95
SBR 1500	5
Magnesium Oxide	5
Cadmium Oxide	4
FEF Carbon	30
SRF Carbon	30
MT Carbon	30
Di-2 Butyl Hexyl Azelate	5
Dioctyl Sebacate	5
Aminox Antioxidant	1
Zenite Antioxidant	1
Lupersol 101 Peroxide	1.5
Total Parts	<u>212.5</u>

Cure: 5'/188°C (370°F)

* MIL-P-83461 formulation uses Krynac 27.50.

<u>**Compound</u> <u>14919-25</u>	<u>Nitrile</u> <u>Polymer</u>	<u>Mole-%</u> <u>ACN</u>
-1	Krynac 27.50	27
-2	Krynac 34.50	34
-3	Krynac 40.65	40
-4	Krynac 50.75	50

Compound 14919-25-5: National O-Ring Company's 89D8 made from Nippon Zeon's HSN Zetpol 2010; 39% ACN.

Table 24. Tensile Properties of Nitriles Aged
in N1010-250 Thinner at 71°C (160°F)

Compound		M ₁₀₀ psi	M ₂₀₀ psi	M ₃₀₀ psi	T _B psi	E _B %	Shore A	% Area Retained
Krynac 27.50 (14808-54-1)	Aging Period, Weeks							
	virgin	2564	--	--	4821	195	78	--
	1	--	--	--	3084	80	83	26.2
	2	--	--	--	3402	85	83	30.8
	4	3368	--	--	3368	100	87	35.8
	6	3000	--	--	3200	105	88	38.2
Krynac 34.50 (14808-54-2)	virgin	2987	--	--	5383	185	83	--
	1	2667	--	--	3576	145	78	52.1
	2	2419	--	--	3707	150	76	55.8
	4	1916	3855	--	4293	205	80	88.4
	6	1888	3900	--	4186	215	81	58.4
Krynac 40.65 (14808-54-3)	virgin	2734	5000	--	5165	215	80	--
	1	1900	3600	--	3900	200	79	70.2
	2	1877	3900	--	4000	210	77	75.6
	4	1571	3457	--	3902	220	78	77.3
	6	1421	3629	--	4010	215	79	74.9
Krynac 50.75 (14808-54-4)	virgin	1500	2506	3250	3800	445	84	--
	1	1178	2454	2847	2945	300	81	52.3
	2	1086	2173	2800	2963	320	74	56.1
	4	921	1939	2650	2826	375	80	62.7
	6	875	1800	2437	2800	370	81	65.6
Zetpol 2010 (slab 8908)	virgin	4211	--	--	5973	180	93	--
	1	4083	--	--	4865	110	86	49.8
	2	4053	--	--	4907	135	89	61.6
	4	3744	--	--	5128	160	89	76.3

Table 25. Tensile Properties of Compound 14808-54-1
(Krynac 27.50) Aged in 'Spiked' N1010-250
Thinner at 71° C (160° F)

Aromatic 'Spike' and Concentration		M ₁₀₀ psi	M ₂₀₀ psi	M ₃₀₀ psi	T _B psi	E _B %	Shore A	% Area Retained
5% Durene	Aging Period, weeks							
	virgin	2564	--	--	4821	195	78	--
	1	2634	--	--	3805	175	94	70.8
	2	1975	--	--	2981	170	84	53.9
	4	2300	--	--	3000	150	89	47.9
	6	3259	--	--	3663	125	92	48.7
	8	2385	--	--	2943	130	86	40.7
25% Durene	1	2927	--	--	3730	140	87	55.5
	2	2395	--	--	3162	140	88	47.1
	4	2329	--	--	3325	155	87	54.0
	6	2909	--	--	3100	120	90	39.6
	8	2300	--	--	3300	150	83	52.7
5% Mesitylene	1	2847	--	--	3828	160	92	65.2
	2	2600	--	--	3133	130	88	43.3
	4	2783	--	--	3500	140	92	52.1
	6	2894	--	--	3084	120	92	39.4
	8	2534	--	--	3384	155	87	55.8
25% Mesitylene	1	3019	--	--	3623	130	94	50.1
	2	2477	--	--	3097	130	89	42.6
	4	2740	--	--	3397	140	90	50.6
	6	3220	--	--	3510	115	89	42.9
	8	2424	--	--	3223	145	86	49.7
5% Dimethyl-naphthalenes	1	2981	--	--	3776	160	92	64.3
	2	2564	--	--	3478	145	88	53.6
	4	2783	--	--	3578	145	88	55.2
	6	2882	--	--	3180	125	89	42.3
	8	2374	--	--	3396	150	84	54.2
25% Dimethyl-naphthalenes	1	2868	--	--	3905	150	89	62.3
	2	1988	--	--	2882	150	84	46.0
	4	2494	--	--	3221	160	82	54.8
	6	2477	--	--	3219	130	87	44.5
	8	2200	--	--	3300	150	78	52.7

Table 26. Tensile Properties of Compounds 14808-54-2 through -4 (Krynacs 34.50, 40.65, 50.75) Aged in 'Spiked' N1010-250 Thinner at 71° C (160° F)

Aromatic 'Spike' and Concentration		M ₁₀₀ psi	M ₂₀₀ psi	M ₃₀₀ psi	T _B psi	E _B %	Shore A	% Area Retained
Krynac 34.50 in 5% Durene	Aging Period, weeks							
	virgin	2987	--	--	5383	185	83	--
	1	1988	--	--	3692	160	84	59.3
	2	1989	--	--	3254	150	80	49.0
	4	2273	--	--	3586	140	83	50.4
	6	2725	--	--	3111	110	84	34.4
	8	1923	--	--	3322	150	76	50.0
25% Durene	1	1836	--	--	3672	170	88	62.7
	2	1839	--	--	3478	160	79	55.9
	4	1882	--	--	3576	160	84	57.5
	6	3030	--	--	3470	120	83	41.8
	8	1887	--	--	2909	140	70	40.9
Krynac 40.65 in 5% Durene	virgin	2734	5000	--	5165	215	80	--
	1	3765	--	--	4205	110	86	41.7
	2	2230	--	--	4267	160	84	61.5
	4	2491	--	--	3314	110	84	32.8
	6	3619	--	--	4810	140	87	60.6
	8	2746	--	--	4414	160	80	63.6
25% Durene	1	2600	--	--	5095	180	81	82.6
	2	2775	--	--	4347	150	82	58.7
	4	2787	--	--	4439	150	83	60.0
	6	3663	--	--	4894	140	85	61.7
	8	2647	--	--	4499	155	79	62.8
Krynac 50.75 in 5% Durene	virgin	1500	2506	3250	3800	445	84	--
	1	2834	--	--	4752	175	89	49.2
	2	4152	--	--	4216	100	87	24.9
	4	--	--	--	4390	95	88	24.7
	6	--	--	--	3814	80	89	18.0
	8	--	--	--	3300	90	85	17.6
25% Durene	1	3836	--	--	4211	110	90	27.4
	2	3925	--	--	4025	100	86	23.8
	4	4279	--	--	4372	105	84	27.1
	6	--	--	--	3730	70	88	15.4
	8	3879	--	--	4073	105	79	25.3
Zetpol 2010 in 25% Durene	virgin	4211	--	--	5973	180	93	--
	1	5803	--	--	6000	110	94	61.4
	2	5818	--	--	5934	110	90	60.7

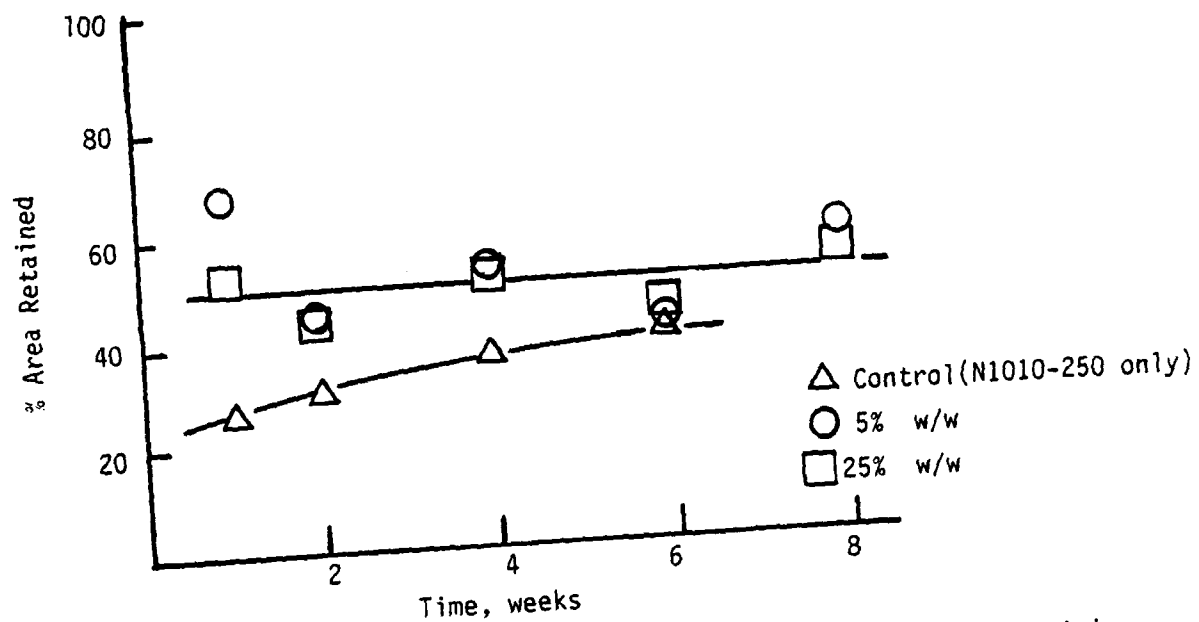


Figure 21. Effect of Aging Krynac 27.50 in N1010-250 Thinner Containing Mesitylene

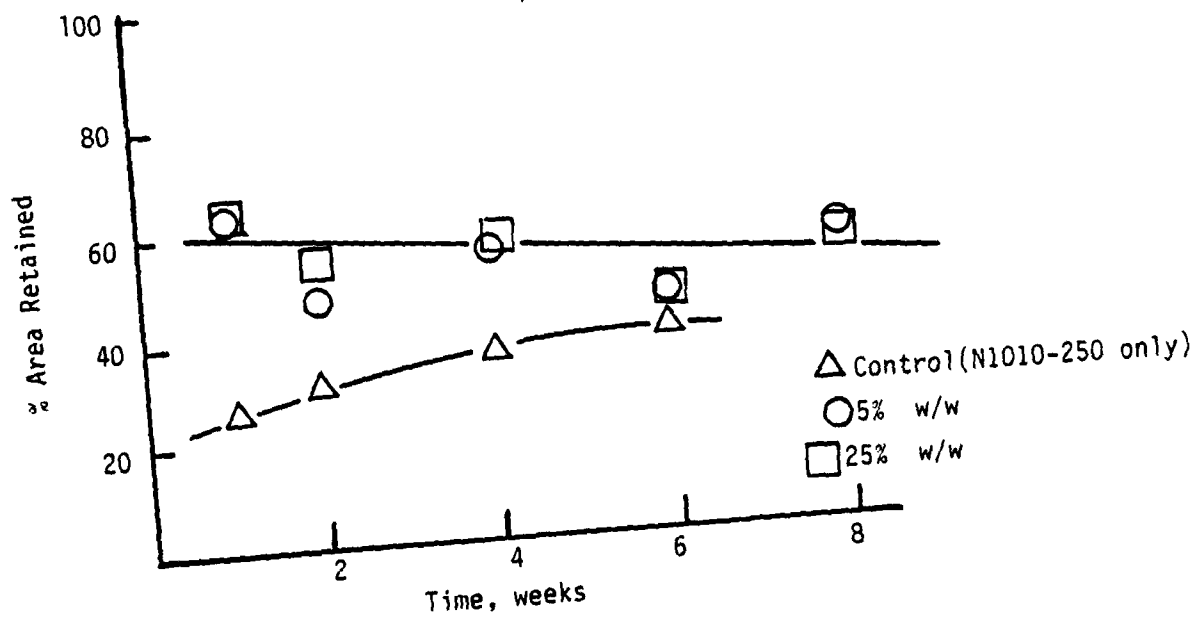


Figure 22. Effect of Aging Krynac 27.50 in N1010-250 Thinner Containing Dimethylnaphthalenes

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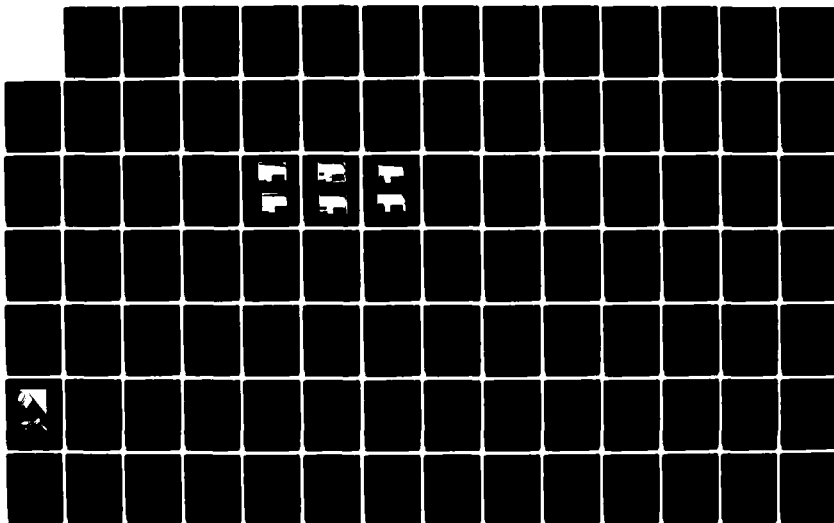
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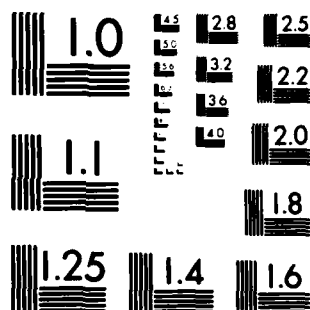
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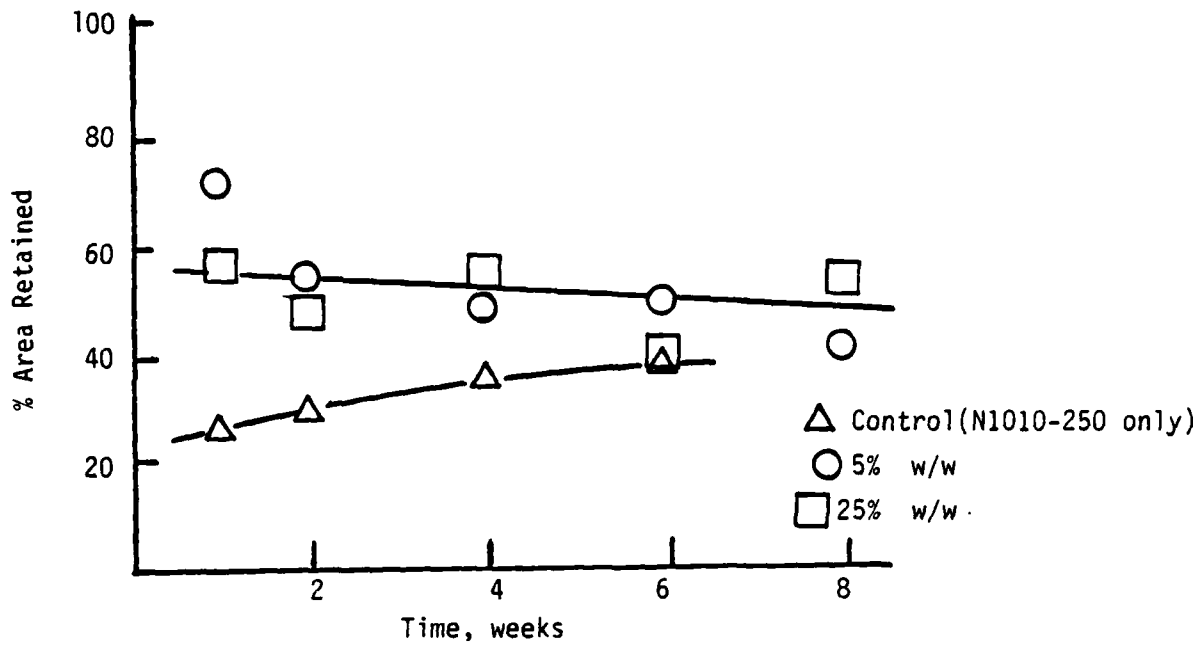


Figure 23. Effect of Aging Krynac 27.50 in N1010-250 Thinner Containing Durene

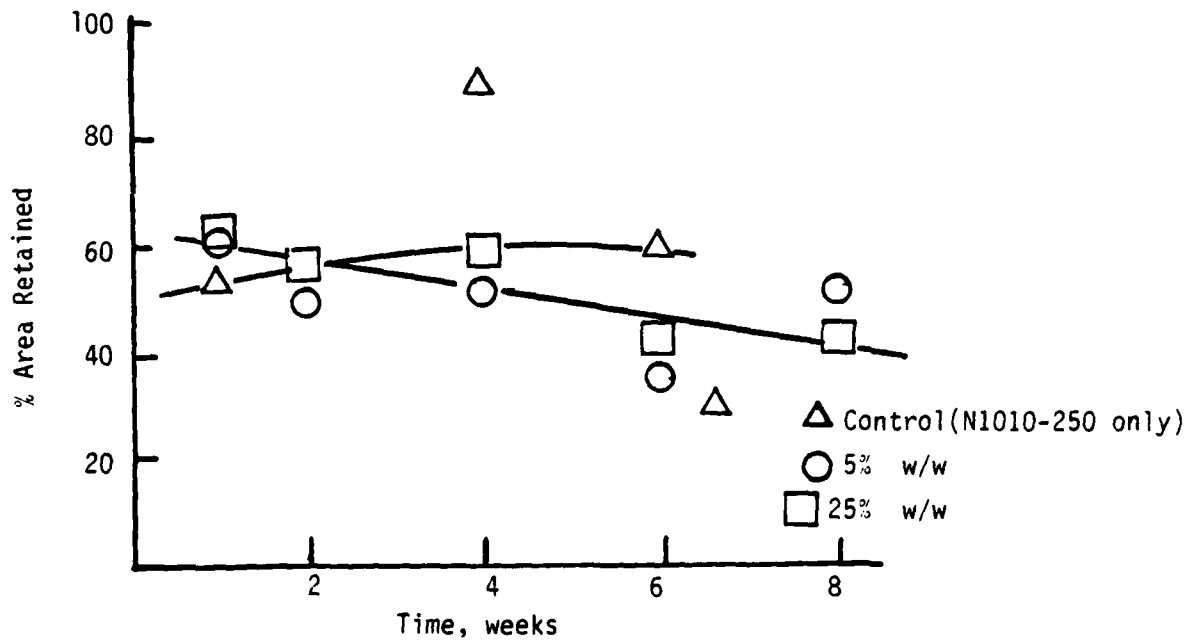


Figure 24. Effect of Aging Krynac 34.50 in N1010-250 Thinner Containing Durene

This may be because the compound is not fully cured after the required cure time.

Figures 25, 26, and 27 show the effects of aging Krynac compounds with acrylonitrile contents of 34, 40, and 50 mole-%, respectively, in durene. Again, in each graph, no difference in property retention is seen by increasing the concentration of durene from 5 to 25%; however, each of these compounds shows the presence of aromatics in the fuel to cause a decrease in the area retained.

Figure 27 depicts the effect of aging the Zetpol 2010 sample obtained from National O-ring in N1010-250 containing 25% durene. No conclusions are drawn from this figure because of the limited aging data.

Figures 28 and 29 show the relationship between acrylonitrile content of the base polymer (Krynac) and property retention of compounds aged in N1010-250 thinner containing 5% and 25% w/w durene respectively. Both graphs indicate an acrylonitrile content of 40 mole-% in Krynac polymers is the best of this group for resistance to degradation. Polymers with ACN contents higher or lower than 40 mole-% exhibited poorer performance upon aging.

5.4 MIXED CURE SYSTEM EVALUATION

Nitriles are conventionally cured with sulfur and may be cured with peroxides. Since sulfur and peroxide attack different sites on the polymer backbone, TRW conducted a study to determine if using a mixed sulfur/peroxide cure system would provide a nitrile compound which is more resistant to attack from peroxides in JP-5 fuel than nitriles cured only with peroxides.

The two compounds listed in Table 27 were prepared for this experiment, samples of which were aged under both rigorous and mild conditions:

- o one week/135°C (275°F) in JP-5 (NFP-14) with an added 150 ppm of di-t-butyl peroxide
- o up to six weeks/71°C (160°F) in JP-5 (NFP-14) with 11.3 ppm peroxide "grown" in the fuel.

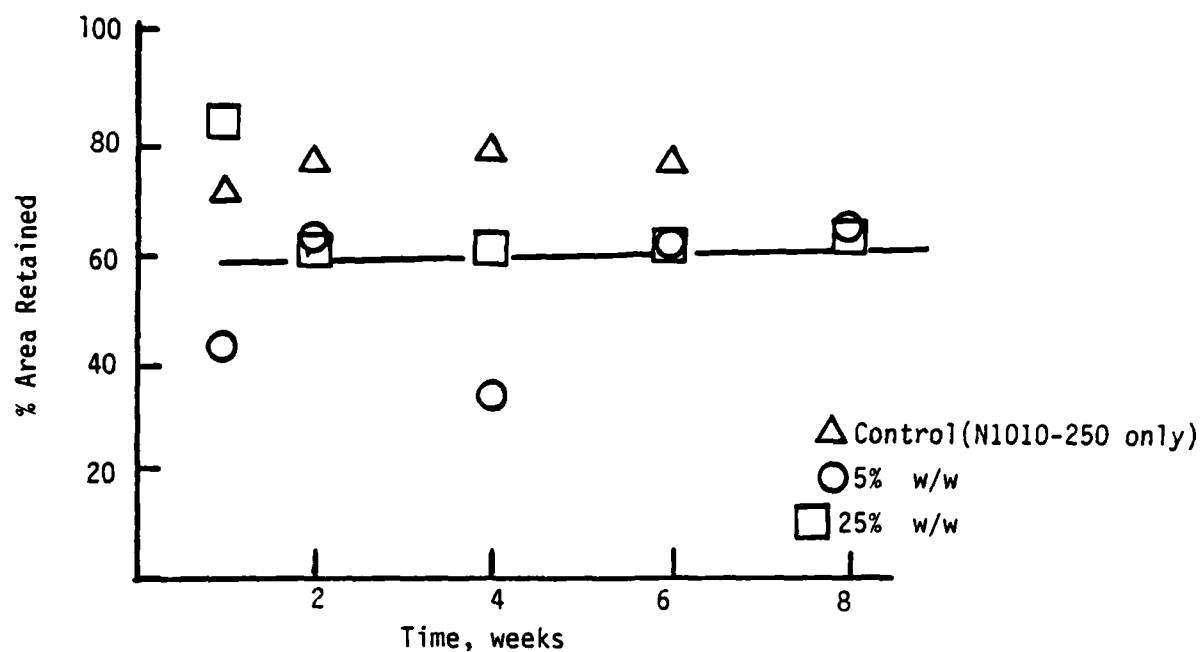


Figure 25. Effect of Aging Krynac 40.65 in N1010-250 Thinner Containing Durene

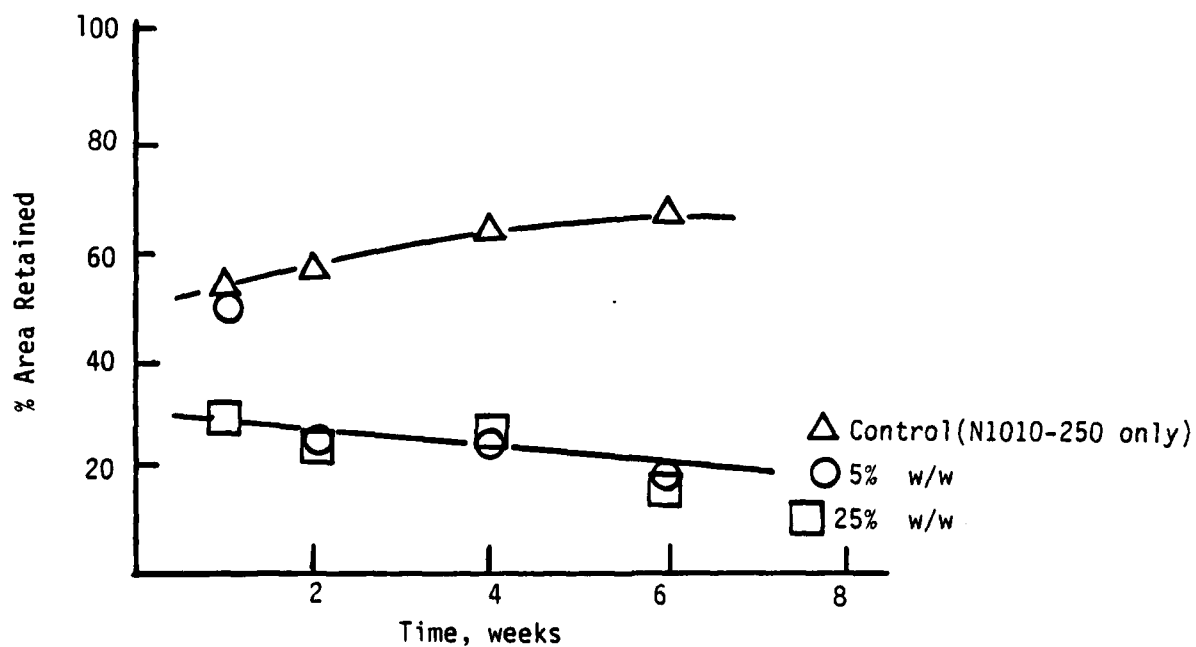


Figure 26. Effect of Aging Krynac 50.75 in N1010-250 Thinner Containing Durene

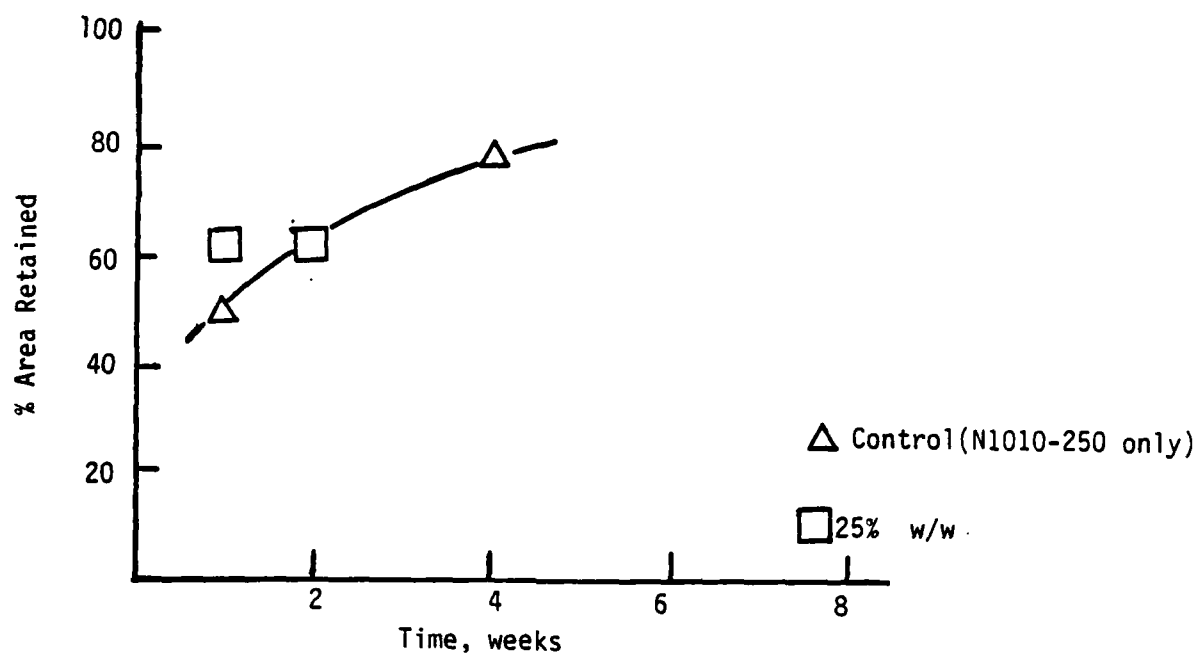


Figure 27. Effect of Aging Zetpol 2010 in N1010-250 Thinner Containing 25% w/w Durene.

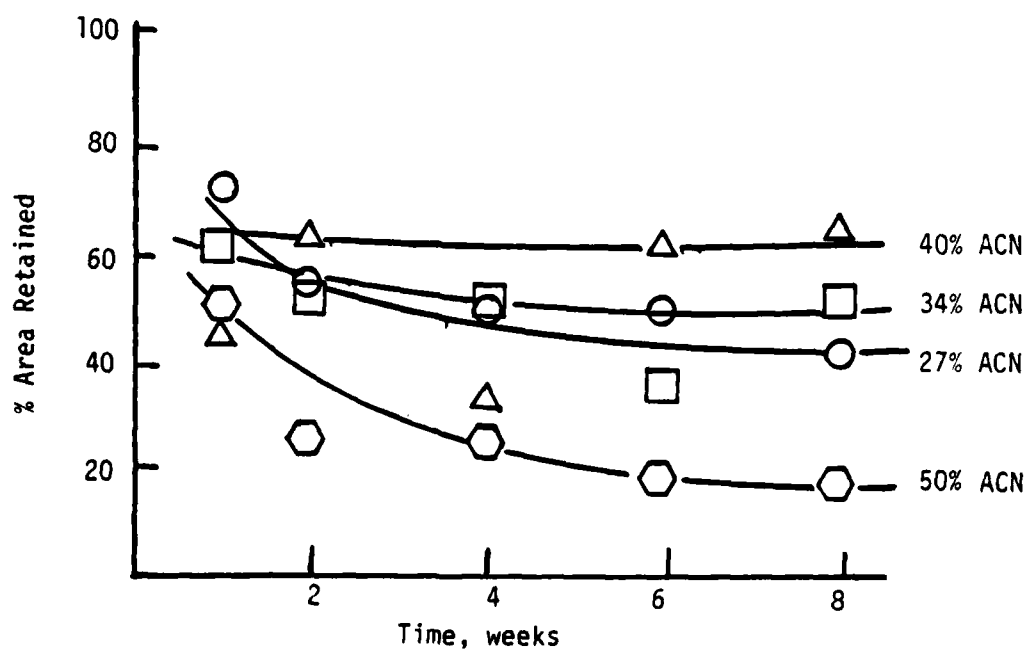


Figure 28. Effect of N1010-250 Thinner Containing 5% w/w Durene on Properties of Krynac Compounds with Varying Acrylonitrile (ACN) Contents

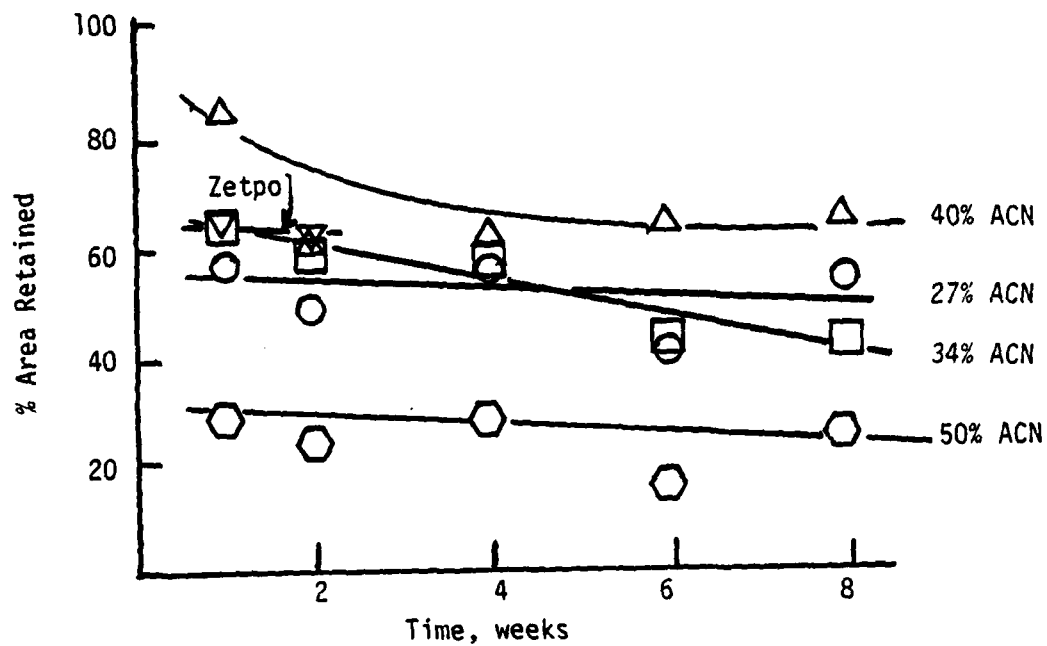


Figure 29. Effect of N1010-250 Thinner Containing 25% w/w Durene on Properties of Krynac Compounds Containing Varying Acrylonitrile (ACN) Contents

Table 27. Evaluation of Mixed Sulfur/Peroxide Cure System in Krynac 27.50
Compound Under Rigorous Aging Conditions

<u>Compound 14808</u>	<u>54-1 (MIL-P-83461</u>	<u>60-1</u>		
Krynac 27.50	95 phr Control)	95		
SBR 1500	5	5		
Magnesium Oxide	5	5		
Cadmium Oxide	4	4		
FEF	30	30		
SRF	30	30		
MT	30	30		
Dimethyl Azelate	5	5		
Dibutoxyethyl Sebacate	5	5		
Aminox Antioxidant	1	1		
Zenite Antioxidant	1	1		
Lupersol 101 Peroxide	1.5	1.7		
Sulfur	--	0.3		
	212.5	213.0		
Cure: 5'/188°C(370°F)				
<u>Tensile Properties</u>	<u>Virgin</u>	<u>Aged*</u>	<u>Virgin</u>	<u>Aged*</u>
M ₁₀₀ , psi	2098	2945	3534	--
TB, psi	3024	3127	3771	4000
EB, %	150	125	110	90
Shore A	86	80	84	80
% Area Retained	--	86.2	--	86.8

*1 week/135°C (275°F) in JP-5 (NFP-14) with 150 ppm di-t-butyl peroxide

Table 27 includes the results from rigorous aging. Table 28 presents the data following aging under mild conditions. Based on percent area retained, the study showed no advantage for using a mixed cure system.

For the rigorous aging above, di-t-butyl peroxide was used to 'spike' the JP-5, because despite efforts to "grow" peroxides in NFP-14 identical to the procedure used for successfully "growing" peroxides in NFP-2*, a peroxide level greater than 5 meq/l (40 ppm) could not be reached.

However a comparison of the area retained for the MIL-P-83461 control in Table 27, with the area retained for an identical compound in Table 15 of Section 5.1, suggests that di-t-butyl peroxide is not a good "referee" peroxide for those peroxides naturally grown in JP-5. The compound in Table 27 retained 86% of its original stress-strain area, whereas the one in Table 15 exposed to an equivalent amount of naturally "grown" peroxides only retained 13% of its original area.

Two areas therefore remain to be addressed:

- o what does NFP-14 contain [probably an antioxidant(s)], that NFP-2 does not, which gives the former resistance to "growing" peroxides?
- o is there a good "referee" peroxide that could be used as a basis for a quality control specification?

5.5 EVALUATION OF NIPPON ZEON'S HIGHLY SATURATED NITRILE POLYMERS

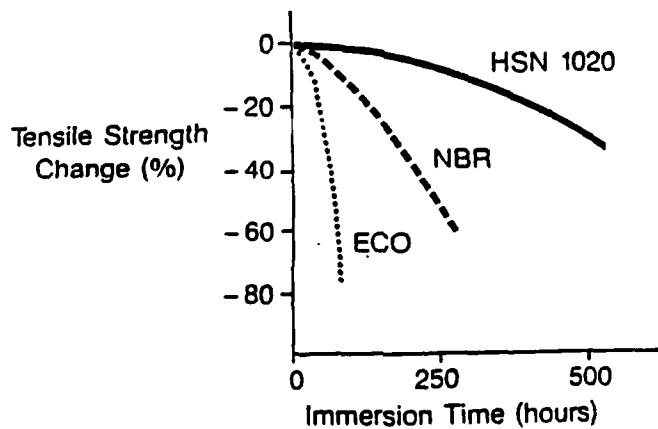
Hashimoto et. al. (Nippon Zeon Co., Ltd) recently reported⁽¹¹⁾ on new highly-saturated nitriles (HSN). The authors state that HSN is made by hydrogenating nitriles to produce a saturated backbone, and are therefore expected to overcome the weaknesses of conventional nitriles. Figure 30 is taken from the Hashimoto paper as an example in which samples of a conventional nitrile rubber containing 41% ACN (NBR), epichlorohydrin-ethylene oxide copolymer (ECO), and HSN 1020 (ACN content of 45%) were aged at 60°C (140°F) in ASTM fuel B containing 50 meq/l (400 ppm) of lauroyl peroxide. As shown, the HSN exhibited superior performance than its conventional nitrile counterpart. Samples of the three grades of HSN produced by Nippon Zeon were therefore ordered for evaluation.

*16 hr/100°C (212°F), followed by 7 days/RT

Table 28. Evaluation of Mixed Sulfur/Peroxide Cure System
In Krynac 27.50 Compound Under Mild Aging Conditions

	Compound 14808-54-1 Peroxide Cure (MIL-P-83461 Control)					Compound 14808-60-1 Sulfur/Peroxide Cure				
	Virgin	1 Wk	2 Wk	4 Wk	6 Wk	Virgin	1 Wk	2 Wk	4 Wk	6 Wk
M ₁₀₀ , psi	2098	3024	3053	2989	2628	3534	--	--	--	--
TB, psi	3025	3415	3895	3362	3047	3771	4718	3986	3428	3118
EB, %	150	120	145	120	100	110	95	95	90	85
Shore A	86	90	88	84	80	84	88	84	82	82
% Area Ret.	--	90.3	100	88.9	67.2	--	100	91.3	74.4	63.9

Figure 30. Oxidized Fuel B Resistance at 60°C⁽¹¹⁾



The Zetpol polymers were first evaluated in the MIL-P-83461 formulation (see Table 11) to determine if any of the grades could be used as possible "drop-in" substitutes for the Krynac 27.50 conventional nitrile base polymer used:

<u>Compound</u>	<u>Nitrile Base Polymer</u>	<u>Mole-% ACN</u>
14919-25-1	Krynac 27.50	27.5
14919-69-1	Zetpol 1020	45
14919-69-2	Zetpol 2020	37
14919-69-3	Zetpol 2010	37

Triplicate tensile bar samples (D1729 die) of each compound were aged in JP-5 fuel (NFP-14) with an initial peroxide content of 35 meq/l (280 ppm) for one week at 135°C (275°F). Post-test fuel samples were submitted for peroxide analysis. Samples were dried in vacuo 16 hr/80°C (176°F) prior to testing. Tensile properties were measured for both aged and virgin samples. Table 29 compares these results.

The Zetpol 1020 compound (45 mole-% ACN) and the MIL-P-83461 (27.5 mole-% ACN) control were severely degraded, retaining only 4% and 2%, respectively, of their virgin properties. In contrast, both Zetpol 2010 and 2020 compounds (37 mole-% ACN) had excellent (100%) property retention.

These results support the conclusion reached in the aromatic study discussed in Section 5.3, where it was shown that property retention increased with increasing ACN contents up to 40 mole-%, and then decreased.

Concern was expressed over the disfiguring effect of aging on the samples, particularly on the Zetpol 2010 and 2020 compounds. Although recognizably tensile bars, the pre-aging shape (length 4", tab width 5/8", thickness 0.75") was significantly altered; post-aging dimensions ranged from 2.5-3" length, 1/4-1/2" width and 0.09-0.2" thickness. The most substantial alterations were observed for the Zetpol 2010 and 2020 compounds, despite having superior property retention, as discussed above.

As a consequence of the tensile bar results, the question of O-ring behavior under similar aging conditions arose. Therefore, three 2-214 O-rings of each Zetpol compound were aged in JP-5 for one week at 135°C (275°F).

Table 29. Zetpol Polymer Evaluation Study Results

Compound	Unsaturation %	Acrylonitrile Content, mole-%	M ₁₀₀ psi	M ₂₀₀ psi	M ₃₀₀ psi	T _B psi	E _B %	Shore A	Area Retained %	Post-test Peroxide ppm
14919-69-1 (Zetpol 1020)	10	45	1157 --	2120 --	2554 --	2554 926	320 35	84 90	-- 4	11.0
14919-69-2 (Zetpol 2020)	10	37	800 1093	--	--	1299 1610	195 160	78 73	-- 100	1.2
14919-69-3 (Zetpol 2010)	5	37	1016 929	1714 1737	--	1778 1818	220 240	78 68	-- 100	1.6
14919-25-1 (MIL-P-83461)	13	27	2564 --	--	--	4821 727	195 20	78 86	-- 2	1.0

Although the initial peroxide content of the JP-5 was only 2 ppm, each compound underwent obvious physical changes including decreased diameters and increased ring thickness. As demonstrated by the tensile bars, Zetpol 2010 and 2020 O-rings were similarly the most misshapen.

The initial conclusion reached from this evaluation was that Zetpol polymers were inapplicable for use with JP-5 because of the resultant physical deformation, even though excellent property retention was obtained with the grades containing 37 mole-% ACN. However, discussion with Nippon Zeon Sales representatives indicated the peroxide content and cure temperature in the MIL-P-83461 formulation are too high to use with HSN polymers. The deformation noticed was caused by the compounds curing too fast; thus, not allowing adequate time to flow in the mold. Following Nippon's technical data, the polymers were re-evaluated in one of their experimental formulations (Table 30).

The three compounds listed in Table 30 were aged one week at 135°C (275°) in JP-5 (NFP-14) containing 37.5 meq/l (300 ppm) peroxide, 32.5 meq/l (260 ppm) of which was added di-t-butyl peroxide [5 meq/l (40 ppm) "grown in"]*. Following drying at 80°C (176°F) for 16 hours in vacuo to remove residual JP-5, samples were tested for tensile properties. Results are included in Table 30.

All samples retained over 70% of their original properties; however, as indicated by the data in Table 27, this is comparable to the retention of a conventional nitrile (Krynac 27.50) compound exposed to di-t-butyl peroxide. Thus, it cannot be concluded from this data whether or not Zetpol polymers offer superior resistance to naturally occurring peroxides. The data from Table 29, wherein the Zetpol polymers were evaluated as "drop-in" substitutes for conventional nitriles in the MIL-P-83461 formulation however, suggest that Zetpol polymers are superior.

*This test was conducted concurrently with the previous aging study (Section 5.4) with di-t-butyl peroxide. The conclusion that this peroxide is not a good "referee" for naturally grown peroxides was not reached until the end of the study.

Table 30. Formulation and Evaluation of Highly Saturated Nitrile (HSN) Polymers

HSN*	100
Zinc Oxide	5
Stearic Acid	0.5
FEF Carbon	40
Dioctyl Sebacate	20
Agerite Stalite Antioxidant	1.5
Agerite Resin D Antioxidant	1.5
Vulcup R Peroxide	<u>3.5</u>
	172.0

Cure: 15'/171°C (340°F)

Postcure: 4 hr/149°C (300°F)

<u>*Compound 14808-</u>	<u>HSN</u>
69-1	Zetpol 2010
29-3	Zetpol 1020
69-4	Zetpol 2020

Tensile Properties of Zetpol Compounds

Compound	69-1		69-2		69-3	
	Zetpol 2010		Zetpol 1020		Zetpol 2020	
	Virgin Aged		Virgin Aged		Virgin Aged	
M ₁₀₀ , psi	533	1416	1000	2100	921	1269
M ₂₀₀ , psi	1417	2633	2200	2638	1209	--
M ₃₀₀ , psi	2880	3549	2314	--	--	--
T _B , psi	5197	4876	2418	2824	1467	1610
EB, %	475	395	335	205	215	140
Shore A	63	78	79	91	79	89
% Area Retained	--	78.0	--	71.5	--	71.5

5.6 PEROXIDE GROWTH IN JP-5 FUEL

As much of the analysis and evaluation of nitrile and alternative polymer systems involved aging in JP-5 fuel, it became desirable to know the rate of peroxide growth in the fuel independent of elastomer contact. Four temperatures were selected for aging: 24°, 71°, 100°, and 135°C (75°, 160°, 212°, and 275°F, respectively).

JP-5 (NFP-1) was selected for testing; however due to experimental error, the set at 71°C (160°F) had to be restarted using Exxon JP-5 (NFP-2), as the NFP-1 was depleted. Two sets of fluids were aged in test tubes. One set contained virgin JP-5, and the other contained JP-5 saturated with MnO₂.

Figure 31 and 32 show the peroxide contents of the NFP-1 fuel as a function of time, for the JP-5 and JP-5 containing MnO₂, respectively. Figure 33 shows the rate of peroxide formation at 71°C (160°F) for NFP-2, JP-5. As indicated, the two fuel samples appear quite different in terms of resistance to peroxide growth.

The peroxide content in the Powerine NFP-1 fuel rose, with the maximum initial peroxide content increasing to about 1 meq/l (8 ppm) as the temperature increased. After about eight hours, the content fell sharply and leveled out between zero and two ppm after about 48-56 hours, with the higher temperatures having lower peroxide contents. One would expect the reverse to be true - the higher the temperature, the higher the peroxide level.

In contrast, at 71°C (160°F), the Exxon NFP-2 fuel continued to rapidly grow peroxide until about 168 hours, at which point it leveled out above 125 meq/l (1000 ppm). A check of the fuel sources indicated that NFP-1 contains an antioxidant(s), whereas the NFP-2 sample does not.

The data from the two fuels were input into the TRW/TSS Computer's Curvfit Program to determine rate equations for the curves plotted. One could not be fit to the NFP-1 fuel; however, an excellent fit was found for the NFP-2 fuel.

$$\begin{aligned} \text{As Received JP-5: } \text{ppm peroxide} &= 15.9 - 3.49t + .10t^2 \quad (71^\circ\text{C}) \\ R^2 &= 0.999 \end{aligned}$$

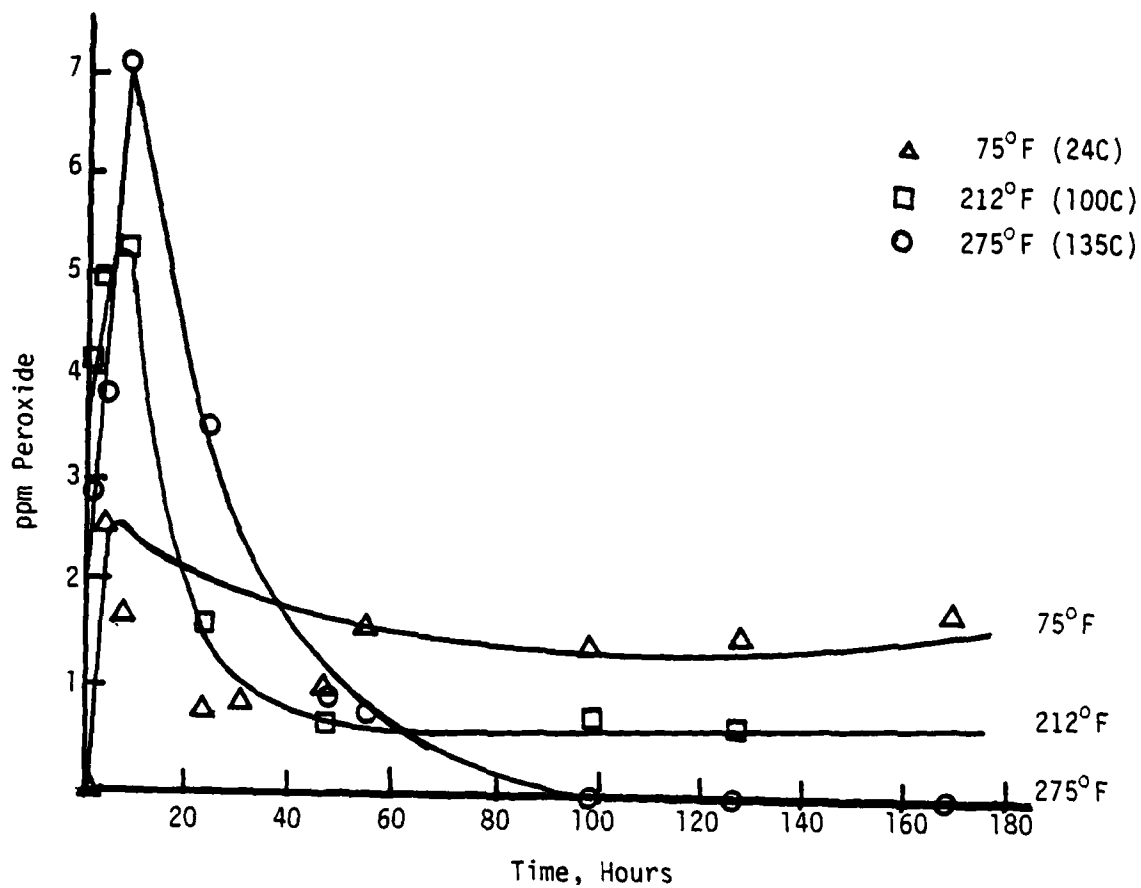


Figure 31. Peroxide Formation in Powerine JP-5 (NFP-1)

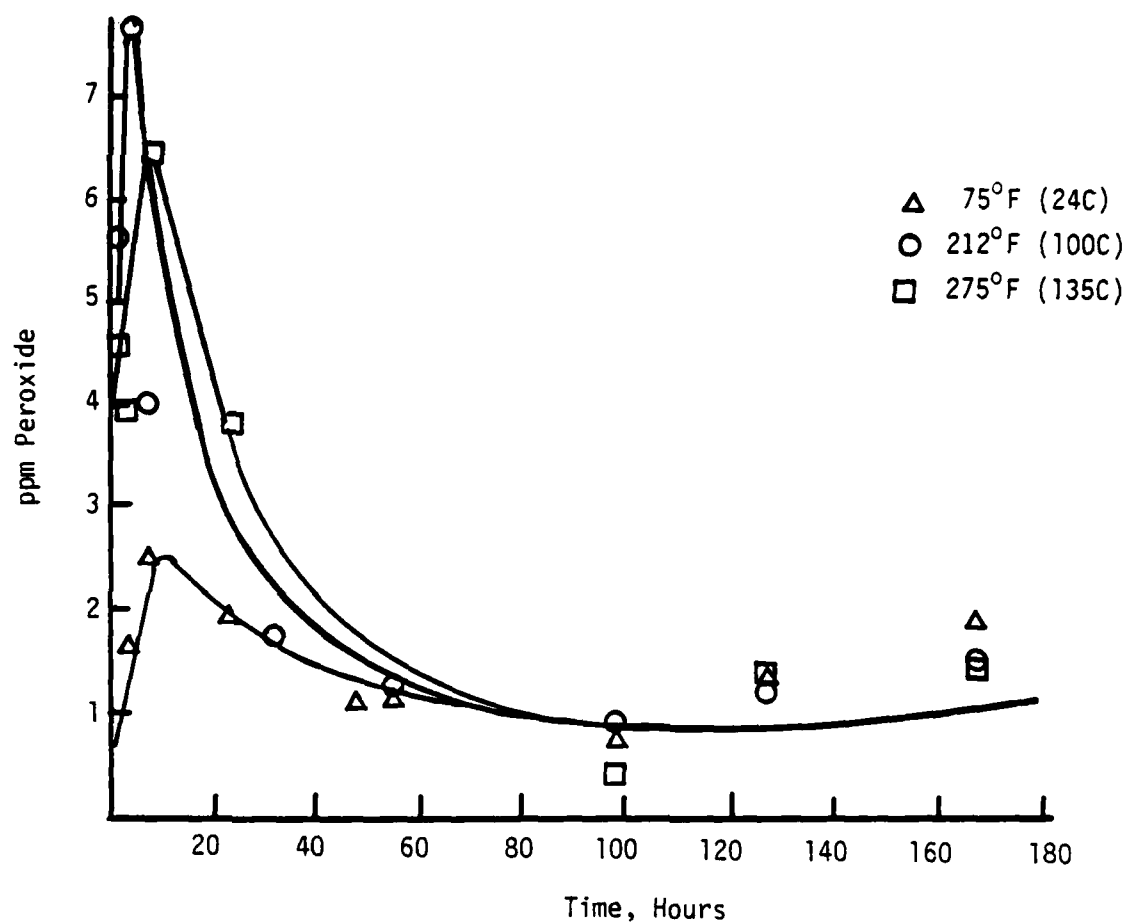


Figure 32. Peroxide Formation in Powerine
JP-5 (NFP-1) Containing MnO_2

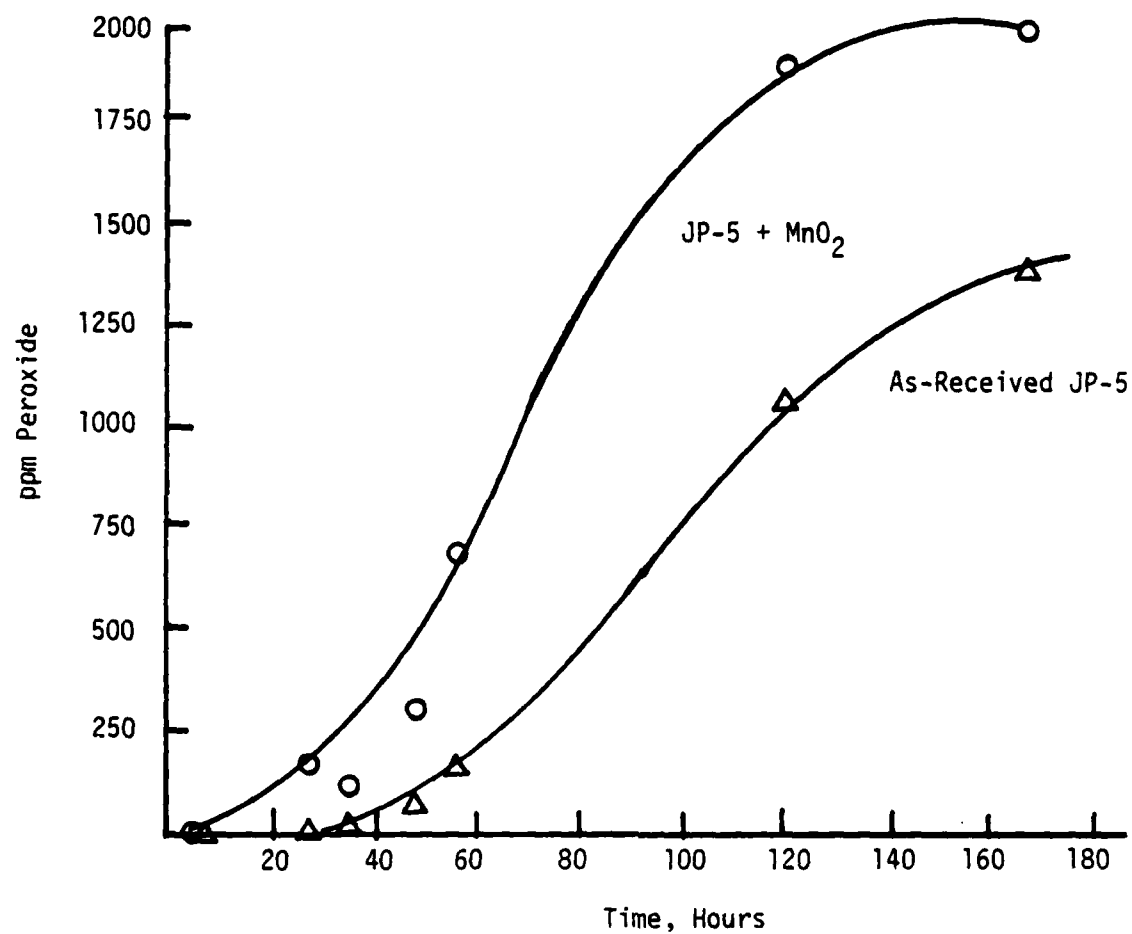


Figure 33. Rate of Peroxide Formation in JP-5 (NFP-2) at 160°F

$$\text{JP-5} + \text{MnO}_2: \text{ ppm peroxide} = 51.8 - 11.3t + .50t^2 - 2.36 \times 10^{-3}t^3 \quad (71^\circ\text{C})$$

$$R^2 = 0.988$$

(In these equations, t is time in hours)

A possible explanation for the shape of the curves for NFP-1 fuel follows. The test tubes used for aging the fuel can hold 30 cc of fuel. In aging studies, approximately 25 cc of fuel are used, leaving 5 cc of ullage containing air. The tubes are capped, and then aged. The initial peak which occurs in Figures 31 and 32 may be peroxide growth initiated by oxygen present in the ullage. Decomposition by antioxidants present in the fuel may be a slow process requiring an induction period of several hours. Thus we see an initial steep rise in peroxide level followed by a sharp decline after 8 hours.

Note that the maximum amount of peroxide grown at 135°C (275°F) was 5.35 ppm or 0.7 meq/liter. This corresponds to approximately 0.133 meq of peroxide in a test tube used to age a rubber specimen. This small amount of peroxide causes severe degradation in nitriles, as noted earlier.

5.7 ALTERNATIVE POLYMER SYSTEM: PNF-280-009

Firestone PNF-280-009 was identified as an alternative polymer for nitrile seals. PNF-280-009 is a silica-filled phosphonitrilic fluoroelastomer that is sold fully compounded (i.e., ready to mold). Samples of the compound were aged under rigorous conditions - 1 week/ 135°C (275°F) in JP-5 containing 36.5 meq/l (292 ppm) peroxide. As stated earlier in Table 11, aging a MIL-P-83461 compound in JP-5 containing 18.3 meq/l (146 ppm) peroxide caused severe degradation - the nitrile compound only retained 13% of its original area under the stress-strain curve.

The aged PNF samples were dried 16 hrs/ 80°C (176°F) in vacuo before determining tensile properties. Results are reported in Table 31.

Table 31. Effect of Aging on PNF-280-009*

	<u>Virgin</u>	<u>Aged</u>	<u>% Retained</u>
T _B , psi	1103	874	79
E _B , %	80	55	69
Shore A	85	88	+3 points
S/S Area x 10 ⁻³	44	24	54

*1 week 135°C (275°F) in JP-5 [36.5 meq/l (292 ppm) peroxide]

Compatibility of PNF with virgin JP-5 was also tested according to standard MIL-SPEC tests: 72 hours at both 70°C and 100°C (158°F and 212°F, respectively), followed by 72 hours at ambient temperature. Table 32 reports the data, which shows essentially no degradation of the rubber, but original properties are marginal for dynamic applications. Therefore PNF is only recommended as an alternative for static nitrile seals.

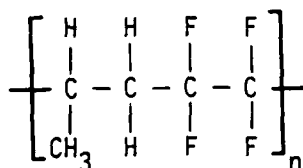
Table 32. Properties of PNF-280-009 Following Aging
72 Hours in JP-5 and 72 Hours in Ambient Air

<u>Property</u>	<u>No Aging</u>	<u>JP-5/70°C</u>	<u>JP-5/100°C</u>
T _B , psi	1103	1025	1230
E _B , %	80	80	75
Shore A	85	82	80
S/S Area x 10 ⁻³	44	41	46
% Area Retained	-	93	104

5.8 ALTERNATIVE POLYMER SYSTEM: AFLAS/EPDM/CTFE TERBLEND

A terblend of Aflas/EPDM/Chlorotrifluoroethylene (polymer/polymer/plasticizer) was developed by TRW under Air Force Contract F33615-82-C-5041 for seals in a high temperature/high pressure hydrocarbon fluid hydraulic system (MIL-H-27601). The terblend will form a seal below -45°C (-54°F), and is stable for several hours at 316°C (600°F).

Aflas is a copolymer of propylene and tetrafluoroethylene, and has the following structure:



Aflas 150

(The structure of EPDM was given in Figure 18). As the blend has no residual polymer backbone unsaturation, TRW postulated that such a blend would also be compatible with JP-5 containing high levels of peroxide, without resulting in degradation of properties.

To test the above theory, the following screening test was conducted. Six compounds varying in EPDM content from 0-25% of the total polymer weight (remaining polymer weight is Aflas) were prepared by physically blending the proper ratios of two masterbatch compounds for Aflas and EPDM. Formulations are listed in Table 33.

The five blends were aged under rigorous conditions which cause severe degradation in conventional nitrile compounds: 1 week/135°C (275°F) in JP-5 containing 36.5 meq/l (292 ppm) of "grown" peroxides. Following aging, the samples were dried under vacuum 4 hr/100°C (212°F), air dried 96 hr/RT, followed by 20 hr/90°C (194°F) under vacuum. Tensile properties were determined per ASTM D412, Shore A hardness measured by ASTM D2240, change in volume (% swell) per ASTM 1460, and TR temperature on the unaged samples per ASTM D1329. Data are listed in Table 34.

As indicated, none of the compounds exhibited any significant degradation, indicating an Aflas:EPDM blend could provide an alternative polymer system. Studies thus turned toward optimization of the blend's properties.

5.8.1 Optimization of Compression Set for Aflas/EPDM Blends

The baseline for optimization of compression set was provided from the Air Force Program. On Contract F33615-82-C-5041, three blends of Aflas/EPDM

Table 33. Compositions of Aflas/EPDM Compounds (14310-23)

<u>-1 Aflas Masterbatch</u>		<u>-2 EPDM Masterbatch</u>	
Component		Component	
Aflas 150P	100	Nordel 1040	100
MT Carbon	30	Cab-O-Sil M5	25
Sodium Stearate	2	Vinyl Silane A-172	1
Triallylisocyanurate	7.5	Agerite Resin D Antioxidant	0.5
DiCup R Peroxide	<u>2.4</u>	B-3000 Resin	25
	141.9	Teflon T-8A	15
		Zinc Oxide	5
		DiCup R Peroxide	<u>2.1</u>
			173.6

Aflas/EPDM Blends (on polymer-to-polymer weight basis)

- 3 95 Aflas/5 EPDM
- 4 90 Aflas/10 EPDM
- 5 85 Aflas/15 EPDM
- 6 80 Aflas/20 EPDM
- 7 75 Aflas/25 EPDM

Cure: 30'/177°C (350°F) → 4 hr/177°C (350°F) *in vacuo*

Table 34. Tensile Properties of AFLAS/EPDM Blends

Compound 14310-23	Unaged					TR ₁₀ (°C)	Aged*					ΔV (%)	% S/S Area Retained	Peroxide in Post-test Fuel (ppm)
	M ₁₀₀ (psi)	M ₂₀₀ (psi)	T _B (psi)	E _B (%)	Shore A		M ₁₀₀ (psi)	M ₂₀₀ (psi)	T _B (psi)	E _B (%)	Shore A			
-1 100% AFLAS	595	1838	2335	270	78	-59.0	499	1506	2155	290	78	43.5	99	109
-3 95% AFLAS	1105	2059	2165	220	85	-53.0	989	1926	2147	250	84	37.5	113	52
-4 90% AFLAS	1455	2338	2338	200	87	-45.5	1272	--	2082	185	85	37.5	82	43
-5 85% AFLAS	1695	--	2361	160	90	-42.0	1688	--	2289	160	88	37.5	97	34
-6 80% AFLAS	1975	--	2370	130	91	-39.0	1873	--	2470	150	88	40.5	120	35
-7 75% AFLAS	2043	--	2430	130	92	-37.0	2028	--	2628	135	90	37.5	112	33

*1 wk/135°C JP-5 (292 ppm peroxide) then dried 96 hr RT plus 24 hr/90°C in vacuo.

were prepared, that had Aflas:EPDM ratios of 85:15, 90:10, and 95:5, respectively (formulations are listed in Table 35). Each formulation was molded as size 2-214 O-rings, followed by exposure to MIL-H-27601 hydraulic fluid. Compression set was determined according to ASTM D395, Method B, for 24, 48, 72, 96, and 672 hours. As a control, Viton GLT O-rings were also tested. Table 36 lists the resultant values, which are also plotted as a function of time in Figure 34.

While the Viton GLT has significantly lower set than the Aflas/EPDM blends, the difference was developed entirely within the first 24 hours. Plotting the data (Figure 34) shows the GLT compound to have a slope of about 1 percent per day while the Aflas/EPDM blends range from about 3/4 percent per day to about 2 percent per day. In light of the inherent experimental error, these are probably not significantly different. The results were interpreted to mean that the high Aflas figures do not arise from polymer network creep, but rather from an initial mechanical deformation.

As a result of the above data, a study was performed under this program to determine the effect of the following variables on compression set:

- o Use of higher molecular weight Aflas 100H
- o Use of G-1000 resin as a coupling agent (based on technology developed by TRW for AFWAL several years ago (AFML-TR-78-71);
- o Use of Austin Black 325 filler instead of MT Black;
- o Extraction of O-rings with Freon TF prior to testing to remove low molecular weight residuals.

Table 37 lists the formulations considered.

One slab and eight 2-214 O-rings were made per compound. Tensile properties were determined per ASTM D412. Swelling in JP-5 following 72 hours/135°C (275°F) was determined per ASTM D1460. All physical properties are also included in Table 37.

Four O-rings each of compounds -4, -5, and -6 were Soxhlet extracted with Freon TF, followed by drying 16 hours/100°C (212°F) in vacuo. The non-volatile residues (NVR) extracted by the Freon from the three samples were:

Table 35. Compositions of Test Compounds

<u>Component</u>	<u>-1</u>	<u>-2</u>	<u>-3</u>	<u>-4</u>
Viton GLT, Dupont	100	-	-	-
Aflas 150P, Xenox	-	95	90	85
Nordel 1040, Dupont	-	5.0	10	15
MT Carbon, Various	30	28.5	27.0	25.5
Cab-O-Sil M-5, Cabot	-	1.3	2.5	3.8
B-3000 Resin, Colorado Chem.	-	1.3	2.5	3.8
Teflon T-8A, Dupont	-	0.8	1.5	2.3
Ca(OH) ₂ , Baker Reagent	4	-	-	-
Diak #7, Dupont	4	7.13	6.75	6.38
Lupersol 101, Wallace & Tiernan	2	-	-	-
Di-Cup R, Hercules	-	2.28	2.16	2.04
Sodium Stearate, Baker	-	1.90	1.80	1.70
Vinyl Silane A-172, Union Carbide	-	0.05	0.10	0.15
AgeRite Resin D, Vanderbilt	-	0.03	0.05	0.08
Zinc Oxide, Baker	-	0.13	0.21	0.34

Table 36. Compression Set of Size 2-214 O-Rings Exposed to MIL-H-27601 at Ambient Temperature

<u>Composition^{a)}</u>	<u>Period of Storage</u>				
	<u>24 Hours</u>	<u>48 Hours</u>	<u>72 Hours</u>	<u>98 Hours</u>	<u>672 Hours</u>
14310-61-1 (GLT)	12.5	14.5	15.5	16.0	21.7
14310-61-4 (95/5)	33.5	34.5	34.5	38.0	45.0
14310-61-5 (90/10)	29.0	30.5	32.5	36.5	41.8
14310-61-6 (85/15)	31.0	33.0	33.5	36.0	39.7

^{a)} -4, -5 and -6 are Aflas/EPDM blends of the indicated ratios.

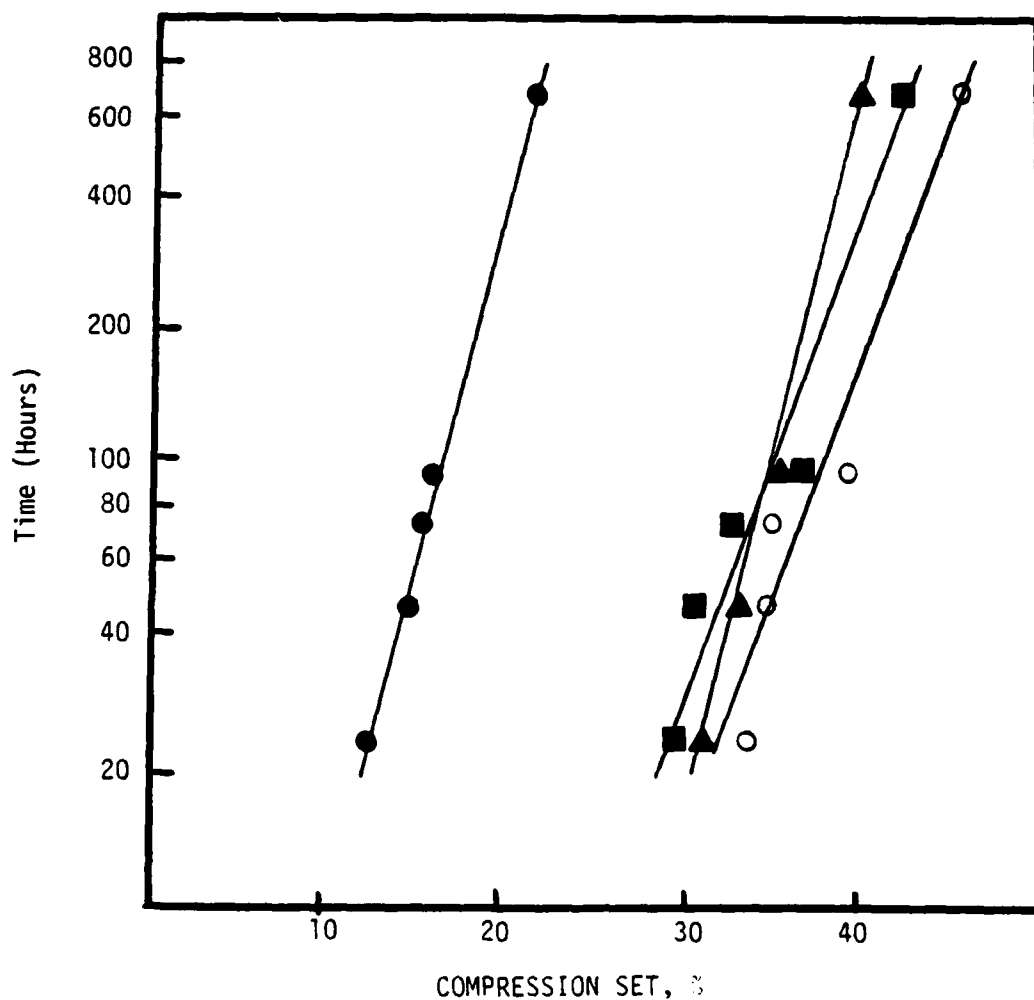


Figure 34. Compression Set of Size 2-214 O-Rings at Ambient Temperature. (● Viton GLT, ■ 90/10 Aflas/EPDM, ▲ 85 Aflas/EPDM, ○ 95/5 Aflas/EPDM).

Table 37. Compounds for Compression Set Study

<u>Component/ Compound 14310-73</u>	<u>-1</u>	<u>-3</u>	<u>-4</u>	<u>-5</u>	<u>-6</u>	<u>-7</u>
Aflas 150P	100	-	-	-	-	-
Aflas 100H	-	100	100	100	100	100
Nordel 1040	-	-	-	-	15	-
Carnauba Wax	-	1.5	1.5	1.5	1.5	1.5
MT Carbon	15	-	-	15	-	-
Austin Black 325	-	20	20	20	20	20
G-1000 Resin*	-	5	5	5	5	-
Na Stearate	2	-	-	-	-	-
Diak #7	7.5	-	4	4	4	7.5
Vulcup R	2	2	2	2	2.5	2

Cure: 15'/370°F

PC : 450°F 16 hr 16 hr 16 hr 16 hr 8 hr 16 hr

*For all compounds except -1 and -7, Austin Black coated 20% with G-1000;
Lot 12931-39 (2/14/78).

<u>Component/ Compound 14310-73</u>	<u>-1</u>	<u>-3</u>	<u>-4</u>	<u>-5</u>	<u>-6</u>	<u>-7</u>
<u>Properties</u>						
M ₁₀₀ , psi	422	500	771	1174	979	770
M ₂₀₀ , psi	1514	930	1542	1849	1663	1649
M ₃₀₀ , psi	-	1180	-	-	-	-
T _B , psi	2116	1274	1793	1897	1775	2015
E _B , %	270	420	270	220	225	260
Shore A	75	78	83	88	83	80
ΔV% JP-5, 72 hr/275°F	48.2	51.3	43.5	37.5	52.9	48.2

<u>Compound</u>	<u>NVR w/w%</u>
14319-73-4	1.36 \pm 0.05
14310-73-5	1.25 \pm 0.07
14310-73-6	1.82 \pm 0.07

Compression set was determined at RT as before on each of the six experimental compounds listed in Table 37, as well as on the extracted O-rings, following 24, 48, 72, and 96 hours.

Figure 35 shows compression set as a function of time for the six baseline compounds. All of the data fit the lines shown within 2 percent. From this, the following is observed:

- o 73-1 has the worse compression set of all compounds, indicating Aflas 100H is an improvement over Aflas 150P.
- o Comparing 73-3 (Baseline G-1000) with -4 (plus the effect of Diak #7) indicates Diak lowers the compression set.
- o -5 shows the effect of adding MT Black to the compounds; compression set is increased.
- o -6 shows the effect of adding Nordel 1040 to the compound; compression set is helped considerably, as this is the only compound showing compression set leveling off at 20 percent.
- o Comparing -7 with -4 shows the effect of adding G-1000 as a coupling agent. The two lines essentially could be superimposed, as they are within experimental error. Thus, G-1000 does not appear to be helpful.
- o Figures 36, 37, and 38 show the effect of extraction on compression set. As indicated, at lower times, the extracted samples have higher compression set values than their respective controls; after longer periods of time, the values are slightly lower. Overall, extraction does not seem to be a useful step.

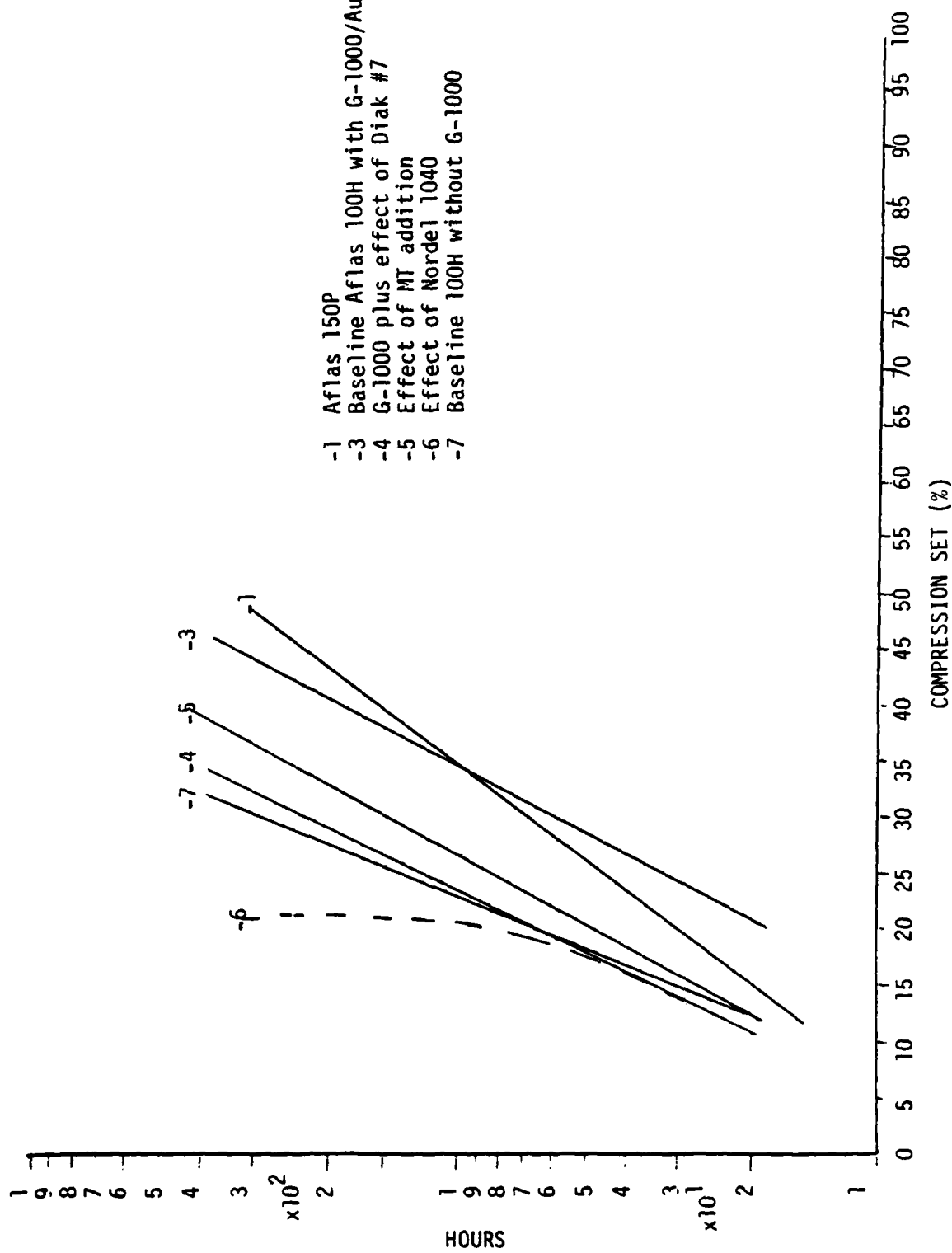
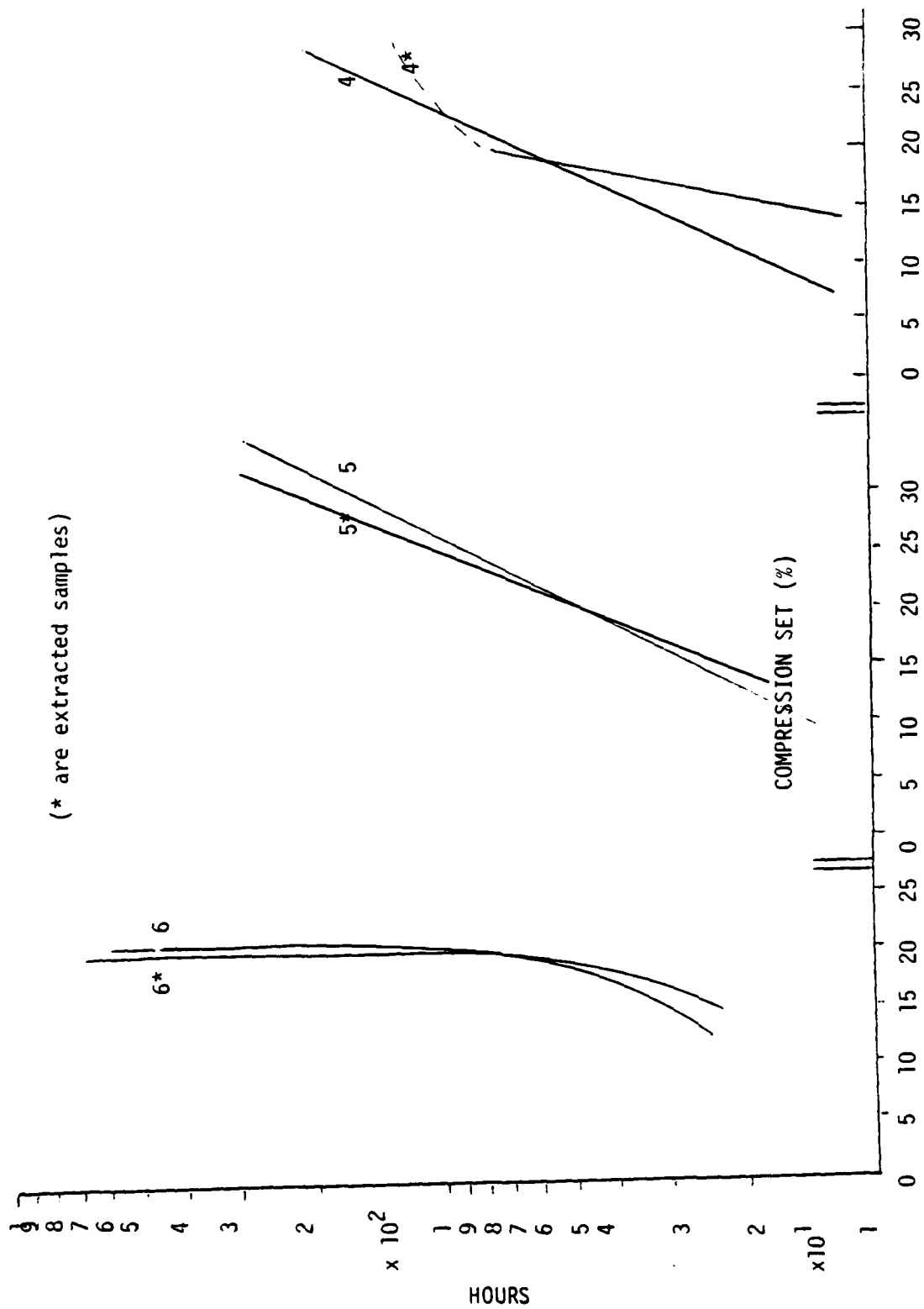


Figure 35. Compression Set vs. Time for Aflas Compounds



As the 73-6 compound had the lowest compression set value, it was the basic compound selected for further study. The G-1000 was omitted for reasons described above. The next experiment performed was aimed at lowering the volume swell of the Aflas/EPDM blend. The original plan was to determine the effects of increasing the Austin Black concentration and adding Teflon T-8A. Four compounds were prepared, Compounds 14310-91-1 through -4, whose formulations are listed in Table 38.

- o In compound 91-1, the Diak coagent was pre-dispersed on the Austin Black before addition to the polymer, and cured properly (see Figure 39).
- o In compounds 91-2 and -3, the Diak was pre-dispersed on the Teflon, before addition to the polymer. Both blistered severely upon curing (Figures 40 and 41).
- o It was thought that the blisters could be caused by poor dispersion of the Diak; thus, the Diak was predispersed on the Austin Black (as in Compound 91-1) before addition to the polymer. Severe blistering again occurred (Figure 42). Thus, it appears that the Teflon was causing the blistering.
- o Compounds 91-5 and 91-6 were prepared with B-3000 resin, which was used to pre-disperse the Teflon before addition to the polymer. Both cured properly without blisters (Figures 43 and 44).

These data show that the addition of Teflon powder to Aflas rubber compounds is impractical without precoating the fluorocarbon powder with a reactive hydrocarbon such as 1, 2-polybutadiene resin.

Tensile properties were determined on Compounds 14310-91-1, -5, and -6. Volume swell was determined in JP-5 following 72 hours/130°C (275°F). Table 38 includes the results. The formulation and properties of Compound 14310-73-6-, which was the baseline for this study, are also listed in the last column for comparison.

Table 38. Aflas:EPDM Compounds for Volume Swell Study

<u>Compounds 14310-91</u>	<u>-1¹</u>	<u>-2²</u>	<u>-3²</u>	<u>-4¹</u>	<u>-5³</u>	<u>-6³</u>	<u>73-6</u>
Aflas 100H	100						→
Nordel 1040	15						→
Carnauba Wax	1.5						→
Austin Black 325	30						20 ⁴
Teflon T-8A		5	10	5	5	10	
B-3000					10	20	
Diak #7	4						→
Vulcup R	2.5						→

Cure: 15'/370°F → 8 hr/450°F

¹Diak pre-dispersed on Austin Black²Diak pre-dispersed on Teflon³Diak pre-dispersed on Austin Black; B-3000 pre-dispersed on Teflon⁴Coated with 5 phr of G-1000

<u>Compounds 14310-91</u>	<u>-1¹</u>	<u>-2²</u>	<u>-3²</u>	<u>-4¹</u>	<u>-5³</u>	<u>-6³</u>	<u>73-6</u>
M ₁₀₀ , psi	676	(See footnote 6)			2005	-	979
M ₂₀₀ , psi	1070				-	-	1663
T _B , psi	1319				2086	2465	1775
E _B , %	280				145	75	225
Shore A	81				93	97	83
ΔV % ⁵	54.5				27.4	19.1	52.9

⁵After 72 hr/275°F (135°C).⁶Extensive blistering made the samples unsuitable for testing.

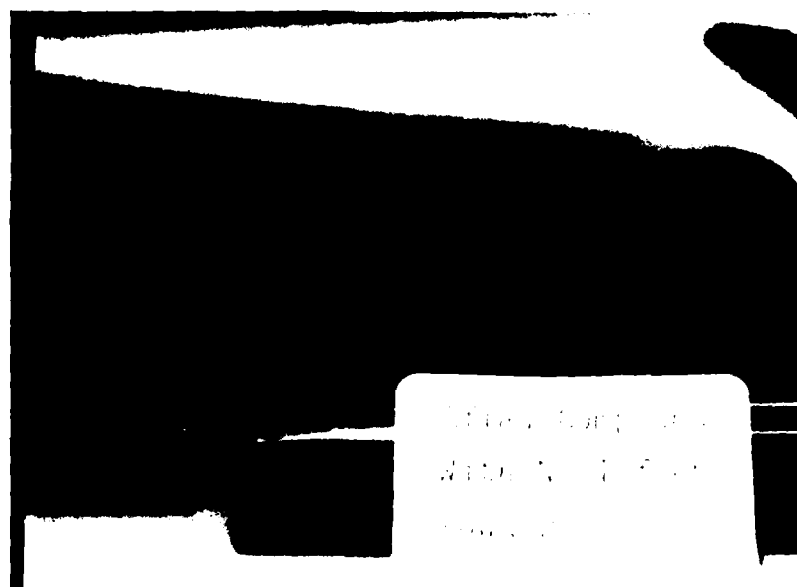


Figure 39. Aflas Compound with Diak Coagent pre-dispersed on Austin Black 325; No blistering upon curing.

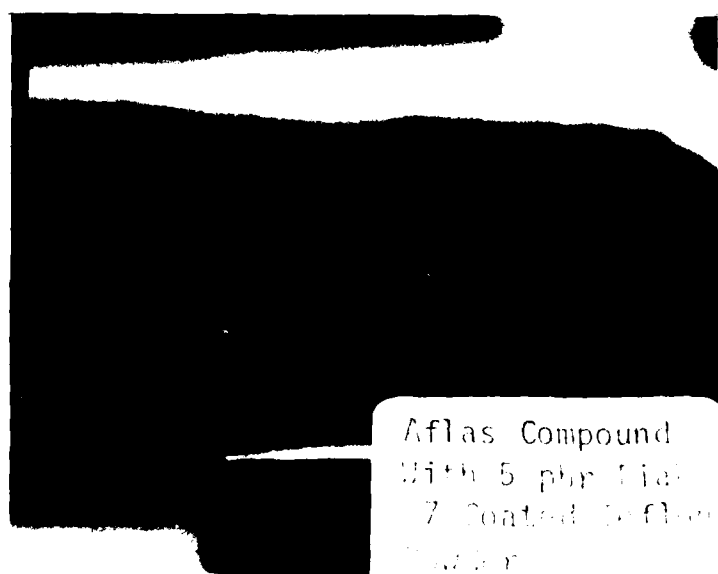


Figure 40. Aflas Compound with Diak pre-dispersed on 5 phr Teflon; Compound blistered upon Curing.

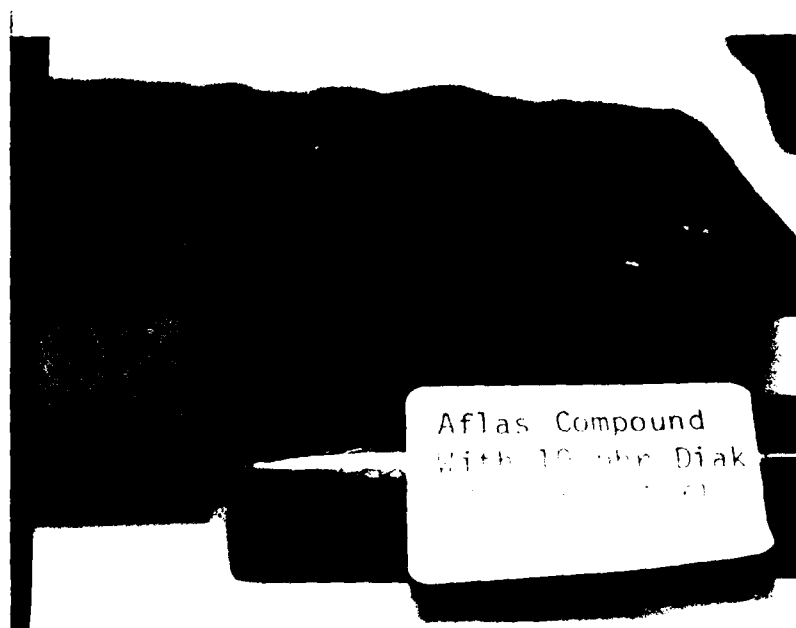


Figure 41. Aflas Compound with Diak Pre-Dispersed on 10 phr Teflon; Compound Blistered Upon Curing.

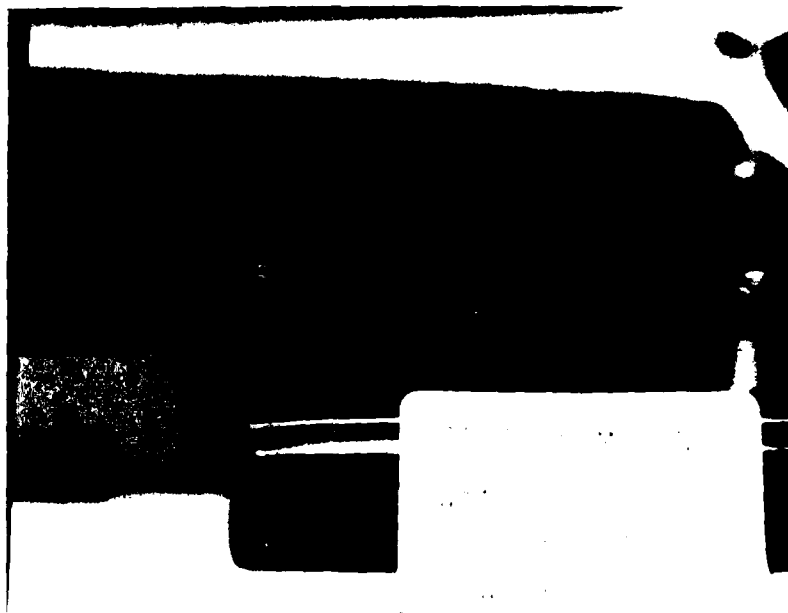


Figure 42. Aflas compound with Diak Pre-Dispersed on Austin Black 325, Teflon Added Separately; Compound Blistered Upon Curing.

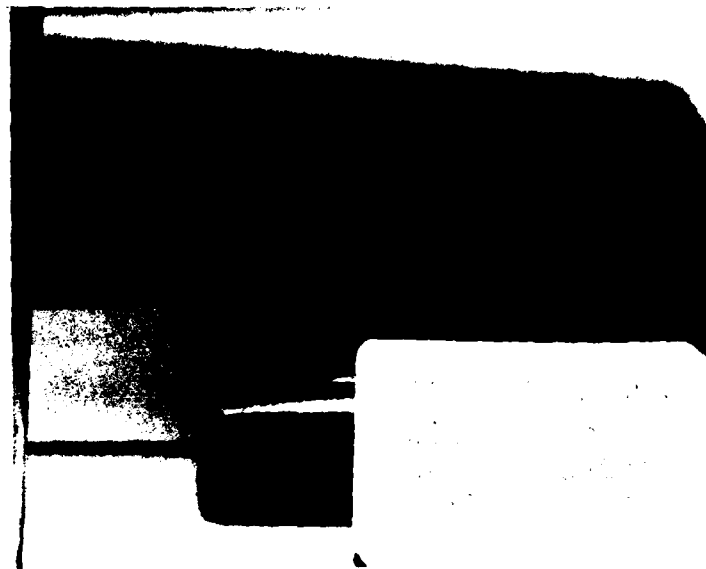


Figure 43. Aflas Compound with B-3000 Resin Coated on 5 phr Teflon; No Blistering Upon Curing.

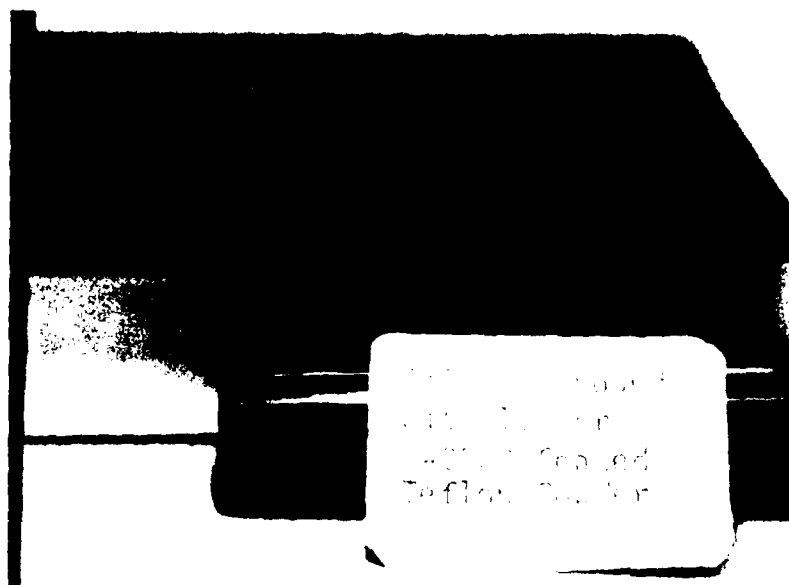


Figure 44. Aflas Compound with B-3000 Resin coated on 10 phr Teflon; No Blistering Upon Curing.

The following observations can be made from the data in Table 38:

- o Comparing the properties of Compound 14310-91-1 with those of Compound 14310-73-6 indicates that increasing the Austin Black concentration hurts tensile properties without affecting the volume swell.
- o Adding Teflon T-8A coated with B-3000 effectively lowers the volume swell; however, 10 phr Teflon:20 phr B-3000 is too high a level, as elongation was negatively affected.

5.8.2 Reduction of Volume Swell of Aflas/EPDM Blends in JP-5

The compounds evaluated during the compression set study (Section 5.8.1) provided the baseline for experimentation to lower the volume swell of Aflas/EPDM blends in JP-5. Specifically, the compression set study indicated:

- o increasing the Austin Black 325 concentration negatively affected tensile properties, yet had no effect on volume swell.
- o Teflon T-8A coated with B-3000 resin effectively lowers volume swell; however, previous concentrations tested were too high as elongation was negatively affected.

Thus Compound 14919-21 was prepared (formulation listed in Table 39), which has concentrations of Nordel 1040, Austin Black 325, B-3000 resin, and Diak #7 lowered from those tested in previous formulations. Table 39 also compares the properties of this compound with those of Compound 14310-91-5. (The latter compound was the most optimized to date, but did not have adequate elongation). As indicated, lowering the four concentrations above negatively affected volume swell, due to a decrease in crosslink density. However, tensile properties are more than adequate.

Based on the properties of the above compounds, it did not appear possible to reduce the swell of an Aflas/EPDM blend to an acceptable level ($\leq 20\%$) through changes in formulation. An alternative solution is to mold O-rings undersized, then swell to size in JP-5 prior to use. This would be an acceptable solution, provided the properties of the swelled material are "adequate".

To determine what "adequate" properties are, TRW used target values set by the Air Force for hydraulic seal compounds (Table 40)¹⁶.

Table 40. Target Values for Air Force Hydraulic Seal Compounds

<u>Property</u>	<u>Original</u>	<u>Aged* Tested Wet</u>
M ₁₀₀ , psi	600 min	300 min
T _B , psi	1400 min	800 min
E _B , %	140 min	140 min
Shore A	75-85	80%

*72 hrs/135°C (275°F) in CTFE plus 1/2 hr/RT in fresh fluid before testing

An alternative and similar set of criteria to use, are the required properties set forth in specification MIL-P-83461 (Table 41).

To determine if a swelled Aflas/EPDM blend would have adequate seal properties, three compounds whose formulations are given in Table 42 were prepared. Tensile properties were determined for virgin samples, as well as for those swelled 72 hrs/135°C (275°F) followed by 24 hr/RT in JP-5 (NFP-7). Results are included in Table 42.

Table 41. MIL-P-8341 Target Values

Property	Original	Aged Tested Wet* MIL-H-5606	Aged Tested Wet MIL-H-83282
M ₁₀₀ , psi	650 min	—	—
T _B , psi	1350 min	675 min	810 min
E _B , %	125 min	80 min	75 min
Shore A	70-80	+5, -10	+5, -10
C.S. %	—	40 max	45 max
Δ V %	—	20 max	15 max

*70 Hrs/135°C (275°F)

Using either of the criteria in Tables 40 and 41, both compounds 14919-21 and 14919-34-1 in Table 42 are acceptable. The latter compound however, has better overall properties with slightly less swell. Either of these compounds could be molded undersized, swelled in JP-5 before installation, and used as alternatives to nitrile seals.

5.8.3 Plasticizers for Aflas/EPDM Blends

The compound developed under Air Force Contract F33615-82-C-5041, and originally tested as an alternative candidate for nitriles used by the Navy, is a terblend of Aflas/EPDM/chlorotrifluoroethylene (CTFE). CTFE acts as a plasticizer for the Aflas/EPDM polymer blend and lowers the TR₁₀ temperature (ASTM D1329) of the blend by -40°C.

Table 42. Evaluation of Aflas: EPDM Blends

Sample Component	14919-21 Parts by Weight	14310-91-5 Parts by Weight
Aflas 100H	100	100
Nordel 1040	10	15
Austin Black 325	10	30
Teflon T-8A	5	5
B-3000	5	10
Diak #7	3	4
Vulcup R	<u>2.5</u>	<u>2.5</u>
Total Parts	135.5	166.5

Cure: 30'/160°C (320°F) → 8 hr/232°C (450°F)

Tensile Properties

M ₁₀₀ , psi	1187	2000
M ₂₀₀ , psi	1731	-
T _B , psi	1912	2086
E _B , %	280	145
Shore A	87	93
ΔV ¹ , %	43.5	27.4
C.S. ² , %	36	-

¹72 hr/135°C (275°F) in JP-5 (NFP-2)

²72 hr/135°C (275°F) per ASTM D395, Method B

A problem encountered early during the terblend evaluation for Navy applications was the extractability of this low temperature plasticizer, CTFE, by JP-5. To determine the extent of extractability, a 90:10 Aflas 150P:EPDM blend (formulation listed in Table 43) was prepared. Four size 2-214 O-rings of the compound weighing 5.1 grams were swelled in Halocarbon 3.1 CTFE until 3.2 grams of the fluid had been incorporated. The O-rings were then refluxed in JP-5 (NFP-1) in round-bottomed flasks fitted with condensers. Following 24 hours/121°C (250°F), the fluid was decanted and replaced with fresh JP-5 fluid for an additional 24 hours. The rings were then blotted dry, and the final weight determined after drying 16 hours/121°C (250°F) in vacuo.

The O-ring weight change is a result of the combination of two effects: absorption of JP-5 by the O-ring and loss of additives including CTFE from the O-ring during exposure to the JP-5 fluid. The amount of CTFE extracted by each 15 ml aliquot of JP-5 was quantified using the CTFE infrared absorbance band at 1195 cm^{-1} and 0.1 mm solution cells with control JP-5 in the reference beam. All results are summarized in Table 44. Of the 3.2 g of CTFE which had been swelled into the rings, 2.70 g (85.6%) was recovered in the JP-5 extractant, 92% of which was removed during the first 24-hour period.

As it is the CTFE which gives the blend its low temperature properties, attention was directed toward either finding a means of preventing extraction of the CTFE, or finding an alternative solvent that would plasticize the blend, yet not be extracted by JP-5.

Toward the former end, chemical abstracts was searched with the logic of chlorotrifluoroethylene with polymers or oligomers to identify methods for preparation of low molecular weight CTFE. Results pointed to the predominance of 3M Company in this area of technology, as they hold a dozen directly related patents.

The problem of extractability was first encountered on the Air Force program using MIL-H-27601 fluid; therefore, the TRW program manager on that contract contacted 3M, who stated they have previously made vinyl-terminated CTFE. TRW thought that the vinyl group could be bound into the base polymer during cure, thus preventing extraction. Intended application was not discussed with 3M and the Air Force Project Engineer was requested to contact

Table 43. Formulation of Aflas: EPDM Blend
for Extraction Study

<u>Component</u>	<u>Parts by Weight</u>
Aflas 150P	90
Norde1 1040	10
Mt Carbon	27
Sodium Stearate	1.8
Cab-o-sil M-5	2.5
Vinyl Silane A-172	0.1
Agerite Resin D	0.05
B-3000 Resin	2.5
Teflon T-8A	1.5
Zinc Oxide	0.5
DiCup R Peroxide	<u>2.4</u>
Total Parts	138.35

Cure: 30'/177°C (350°F) + 4 hr/177°C in vacuo

Table 44. CTFE Extractability Results

Original Weight of Seals, g	5.1393
Weight of Seals Swelled with CTFE, g	8.3393
Weight of Seals After Extraction, Vacuum Dry, g	5.0609
Weight Change, g	3.2784
CTFE Extracted First 24 Hours, g (%)	2.51 (78.4)
CTFE Extracted Second 24 Hours, g (%)	0.23 (7.2)
Total CTFE Extracted, g (%)	2.74 (85.6)

an identified 3M technical person regarding a sample of vinyl-terminated oligomer for testing under both programs. 3M was not interested in preparing this sample.

In the same vein, the Navy program manager contacted Dr. Kirby Scherer of the University of Southern California (USC) to synthesize a sample of vinyl-terminated CTFE. Dr. Scherer was unable to synthesize the requested sample, but did synthesize a vinyl-terminated fluorinated plasticizer, designated FP. This material, in addition to several other solvents, was evaluated as plasticizers for the blend. Also tested, was a high molecular weight CTFE plastic, Kel-F 800. It was postulated that a higher molecular weight CTFE would not be as readily extractable, however, the question remained whether increasing the molecular weight would decrease its plasticizing ability.

A total of eight materials were evaluated as alternative plasticizers:

- o JP-5
- o Sunpar 2280 (a paraffinic oil)
- o Kel-F 800
- o 3-(heptafluoroisopropoxy)-propyl trichlorosilane
- o 3-(heptafluoroisopropoxy)-propyl trimethoxysilane
- o Bray Oil Company 814Z
- o Freon E6.5
- o Vinyl terminated plasticizer (synthesized at USC)

Structures of the above materials are shown in Figure 45.

The first set of experiments evaluated JP-5, Sunpar 2280, and Kel-F 800 in an 85:15 Aflas:EPDM blend to determine their respective plasticization effects. Formulations are listed in Table 45 along with the compounds' respective physical properties. The tensile properties of Compound 14310-63-2 indicate Sunpar 2280 greatly reduced the crosslink density by consuming the peroxide curing agent.

Samples of each compound were aged 72 hours/135°C (275°F) in virgin JP-5, followed by 48 hours/RT air-drying. Volume swell was determined at 135°C after fluid aging, as well as after air-drying. As shown, the percent swell is extremely high.

NAME	STRUCTURE
3-(heptafluoroisopropoxy)-propyl trichlorosilane	$\begin{array}{c} \text{CF}_3 \\ \\ \text{CF}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}-\text{Cl} \\ \qquad \qquad \qquad \\ \text{CF}_3 \qquad \qquad \qquad \text{Cl} \end{array}$
3-(heptafluoroisopropoxy)-propyl trimethoxysilane	$\begin{array}{c} \text{CF}_3 \\ \\ \text{CF}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}-\text{OCH}_3 \\ \qquad \qquad \qquad \\ \text{CF}_3 \qquad \qquad \qquad \text{OCH}_3 \end{array}$
FP-vinyl-terminated fluorinated plasticizer (synthesized by Dr. Scherer of USC)	$\text{CF}_3-\text{CF}_2-\text{CF}_2-\overset{\text{CF}_3}{\underset{\text{CF}_3}{\text{C}}}-\text{CH}_2-\text{CH}=\text{CH}_2$
Chlorotrifluoroethylene (CTFE)	$\begin{array}{c} \text{Cl} \quad \text{F} \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{F} \quad \text{F} \end{array}$
Vinyl-terminated CTFE	$\begin{array}{c} \text{Cl} \quad \text{F} \\ \quad \\ \text{C} = \text{C}-\text{CH}=\text{CH}_2 \\ \quad \\ \text{F} \quad \text{F} \end{array}$
Sunpar 2280 (Paraffinic Oil)	Proprietary
KC1-F 800	$\left[\begin{array}{c} \text{Cl} \quad \text{F} \\ \quad \\ \text{C} - \text{C} \\ \quad \\ \text{F} \quad \text{F} \end{array} \right]$
Bray Oil 823]	Proprietary
DuPont Freon E6.5	Proprietary

Figure 45. Structures of Potential Placticizers for Aflas/EPDM Blends

Table 45. Evaluation of JP-5, Kel-F 800, and Sunpar 2280 as Plasticizers for Aflas/EPDM

Component/Compound 14310-63	-1	-2	-3
Aflas 150P	85	85	85
Nordel 1040	15	15	15
MT Carbon	30	30	30
Na Stearate	2	2	2
Sunpar 2280	-	20	-
Kel-F 800	-	-	20
Diak #7	7.5	7.5	7.5
DiCup R	2.4	2.4	2.4

Cure: 30'/177°C (350°F) → 4 hr/177°C in vacuo

	<u>Properties (D1729 die)</u>		
M ₁₀₀ , psi	1173	188	1067
M ₂₀₀ , psi	-	563	-
T _B , psi	1280	789	1400
E _B , %	110	255	135
ΔV% ¹	69.3	90.7	67.7
ΔV% ²	23.2	9.8	24.6

¹Measured at 135°C (275°F) following 72 hr/135°C in JP-5.

²Measured at RT following above soak and 48 hr/RT air-drying.

TR₁₀ properties were determined on both virgin and air-dried samples. Figures 46 through 50 are the corresponding graphs. As indicated, all virgin samples had essentially the same TR₁₀ temperature, +2.5°C. Neither Sunpar 2280 nor Kel-F 800 acted as a plasticizer. JP-5 however did lower the TR₁₀ by 15°C; thus it too plasticizes the samples although not as much as low molecular weight CTFE (Figure 51).

The next plasticizer evaluated was obtained from Silar Laboratories in Scotia, New York:

o 3-(heptafluoroisopropoxy)-propyltrichlorosilane

For this study, a silica-filled Aflas/EPDM blend was used. The intent was to coat dried Cab-O-Sil M5 with the above silane to provide pendant heptafluoroisopropoxy groups to sorb into the Aflas/EPDM structure, and lubricate the polymer blend for improved low temperature properties.

The silane was added as a coating to the Cab-O-Sil M5 filler; however, when the coated filler was added to the polymer, the compound blistered upon curing. TRW theorized that HCl was being released as a reaction product, interfering with the peroxide cure. Addition to the formulation of six parts of Ca(OH)₂ and three parts of MgO was intended to neutralize the acidity. Although this compound was less blistered, it also was not usable.

A sample of 3-(heptafluoroisopropoxy)-propyl trimethoxysilane was next obtained from Silar. This compound would release methanol as a reaction product which should not affect the peroxide cure. Sixty grams of Cab-O-Sil M5 was added to a two liter resin kettle containing 1200 ml of hexane to form a thin slurry. Thirty grams of the silane was added dropwise, and the mixture stirred for 1.5 hours at ambient temperature under an inert (argon) atmosphere. Following removal of the hexane on a rotary evaporator, the Cab-O-Sil M5 was transferred to a crystallizing dish and dried for 3 hrs at 71°C (160°F). Upon addition to an Aflas/EPDM blend (formulation in Table 46), the vulcanizate again blistered.

Terry Selin of Silar Labs suggested drying the mixture at a higher temperature to drive off any residual water which could compete with the silane for sites on the Cab-O-Sil. The coated filler was remade, and dried for four hours at 120°C (248°F). No blistering occurred during cure when incorporated into the polymer.

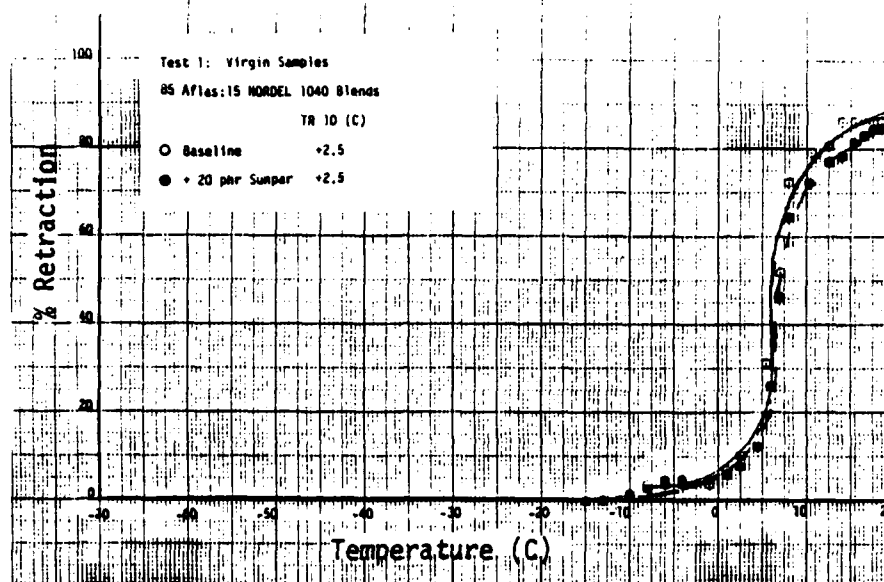


Figure 46. 85:15 Aflas:Nordel 1040 Blends
Baseline and +20 phr Sunpar 2280; TR 10
Curves from Test 1

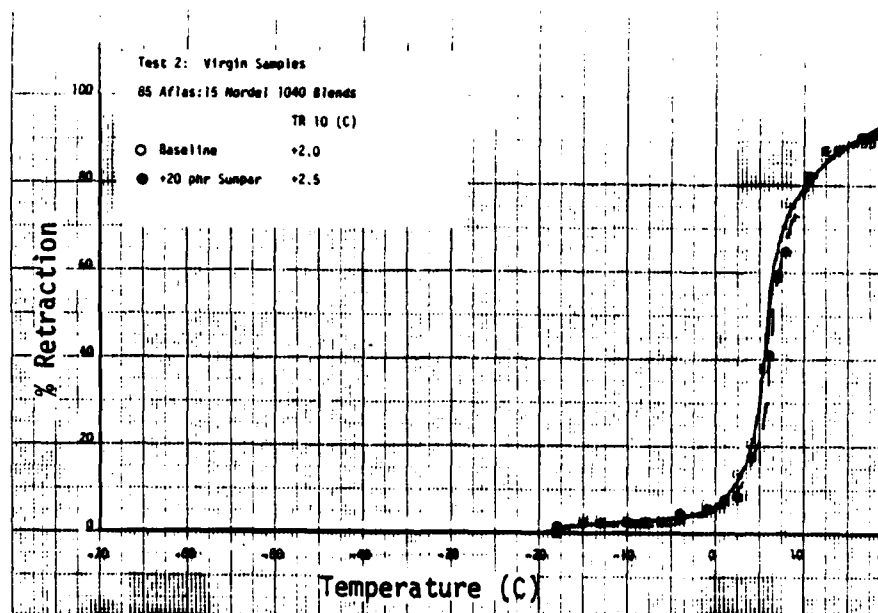


Figure 47. 85:15 Aflas:Nordel 1040 Blends
Baseline and +20 phr Sunpar 2280; TR 10
Curves from Test 2

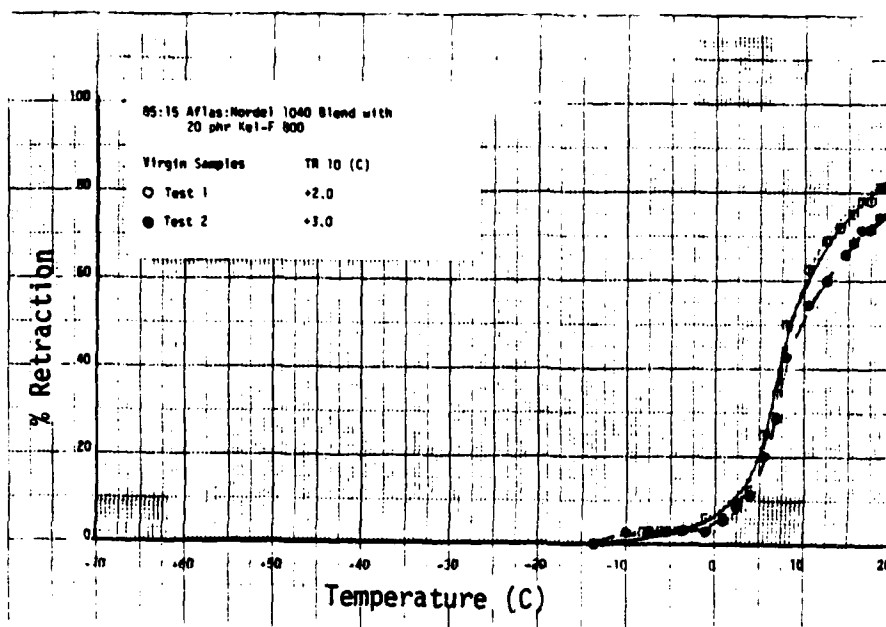


Figure 48. 85:15 Aflas:Nordel 1040 Blends with 20 phr Kel-F 800; TR 10 Curves from Tests 1 and 2

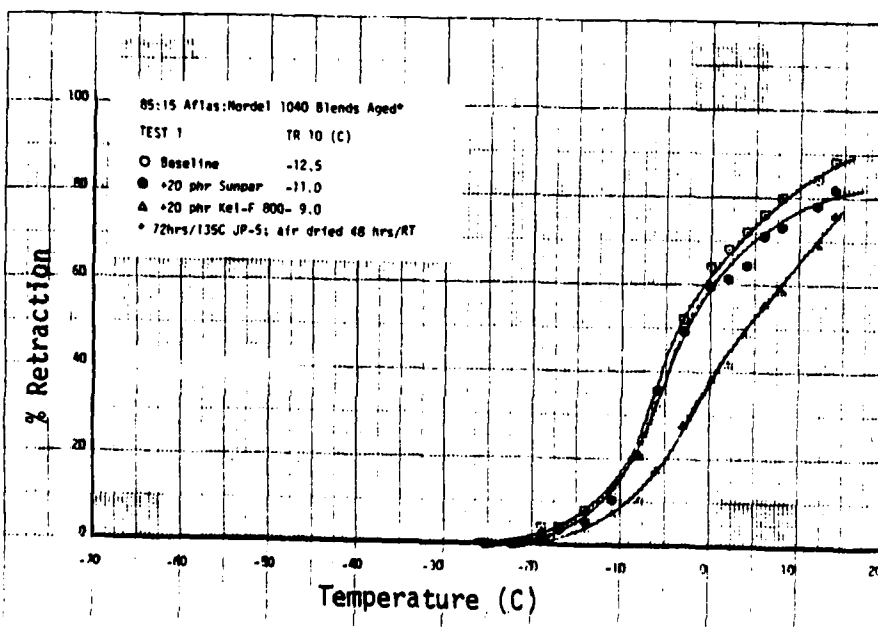


Figure 49. TR 10 Curves for 85:15 Aflas:EPDM Blends Following Aging in JP-5. Test 1.

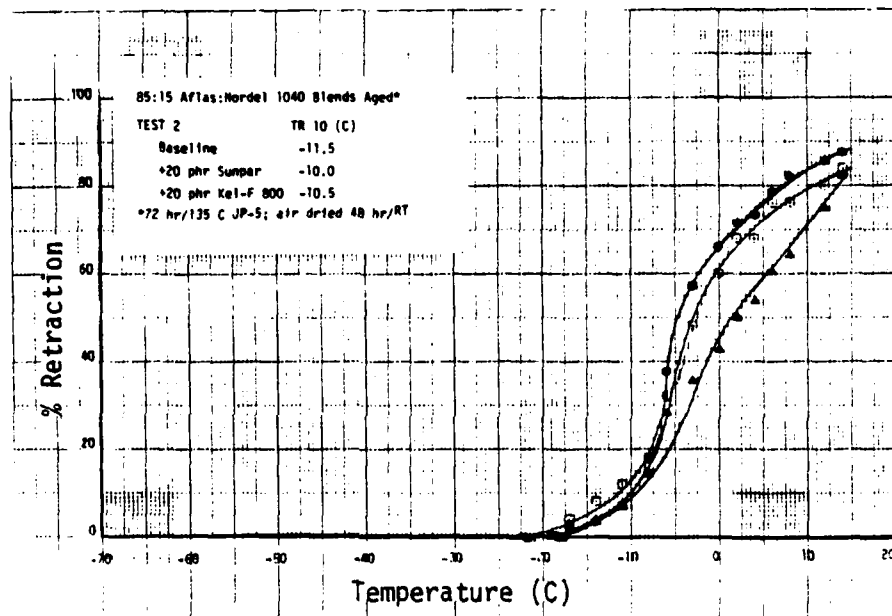


Figure 50. TR 10 Curves for 85:15 Aflas:EPDM Blends Following Aging in JP-5. Test 2.

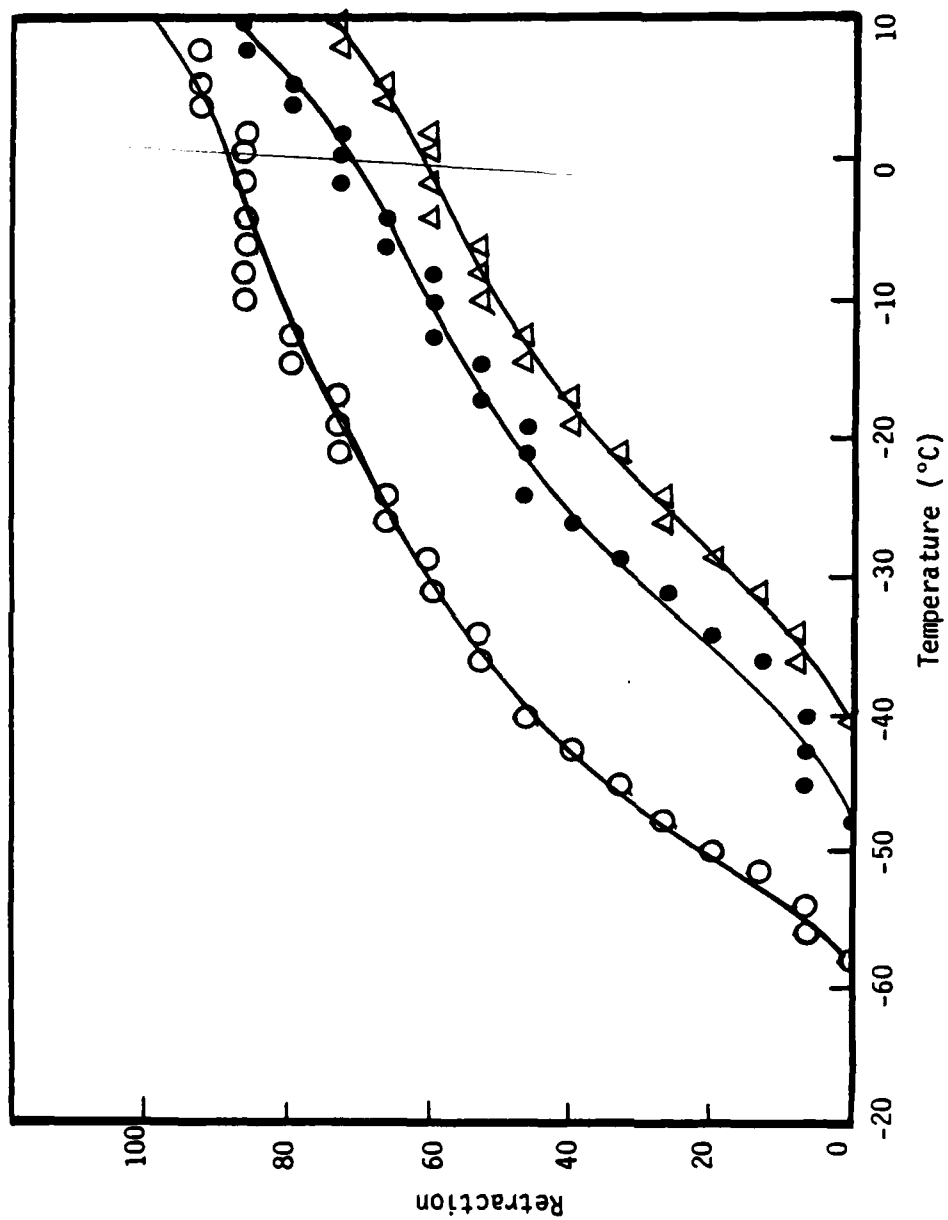


Figure 51. TR_{10} Curves for Various Aflas:EPDM Blends (CTFE Plasticizer)

- 95:5 Blend ($TR_{10} = -53.5^{\circ}\text{C}$)
- 85:15 Blend ($TR_{10} = -40^{\circ}\text{C}$)
- △ 75:25 Blend ($TR_{10} = -33.0^{\circ}\text{C}$)

To determine the silane's ability to plasticize the Aflas/EPDM blend described in Table 46, TR₁₀ tests were performed per ASTM D1329 on virgin samples as well as on those swelled for 48 hours at room temperature in JP-5.

Table 46. Formulation to Evaluate Effect of
Silane Plasticizer in Aflas/EPDM Blend

	<u>Parts by Weight</u>
Aflas 100H	100
Nordel 1040	15
Carnauba Wax	1.5
Sample 14919-48A*	30
Diak #7	1.5
Vulcup R	2.5
Total Parts	<u>150.5</u>

Cure: 30'/160°C (320°F)
Postcure: 8 Hr/232°C (450°F)

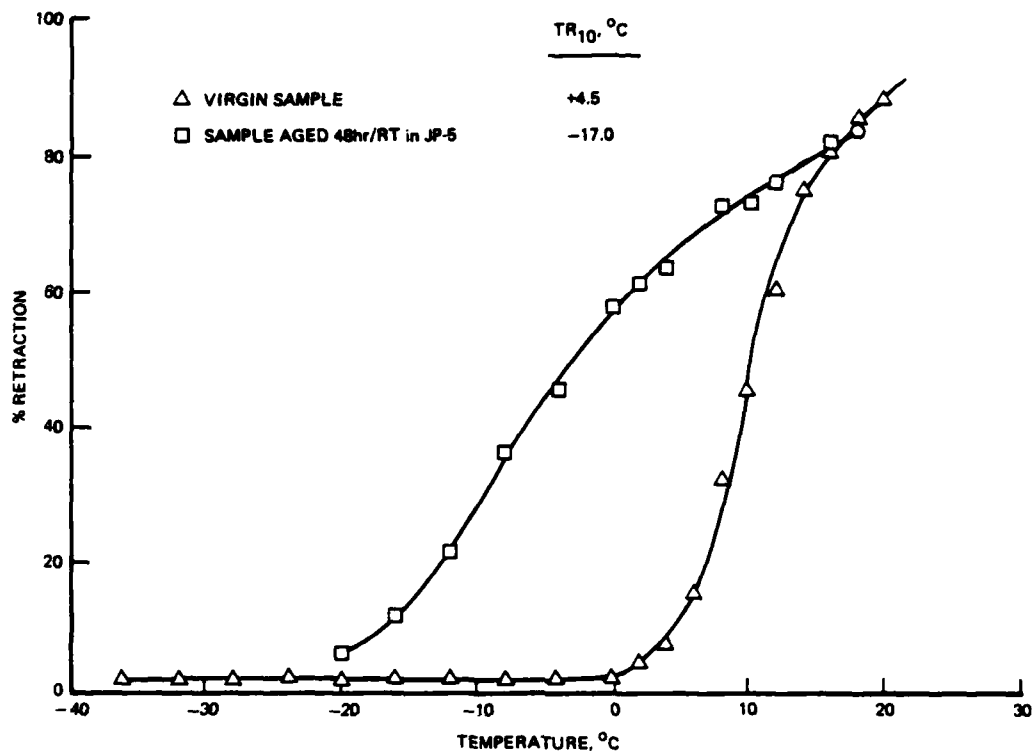
* 20 phr of Cab-O-Sil M5 coated with 10 phr of
3-(heptafluoroisopropoxy)-propyltrimethoxysilane,
Lot 16895.

Figure 52 shows the resultant TR₁₀ curves. The average TR₁₀ temperature of the virgin compound is 5°C (41°F), which is the approximate TR₁₀ of the base polymer blend. Therefore, 3-(heptafluoroisopropoxy)-propyltrimethoxysilane is not an effective plasticizer for Aflas:EPDM blends.

As also indicated in Figure 52, JP-5 lowered the TR₁₀ temperature to -17°C (1.4°F), supporting the result shown in Figures 34 and 35 with an Aflas 150P/EPDM blend - that is, JP-5 acts as a partial plasticizer for Aflas/EPDM blends.

Freon E6.5 and Bray Oil 814Z were next evaluated as alternative plasticizers for the Aflas/EPDM blend described in Table 47. Following postcure of the compound, D1729 tensile bars were placed in each of the two fluids to swell for 120 hours at ambient temperature.

RUN 1



RUN 2

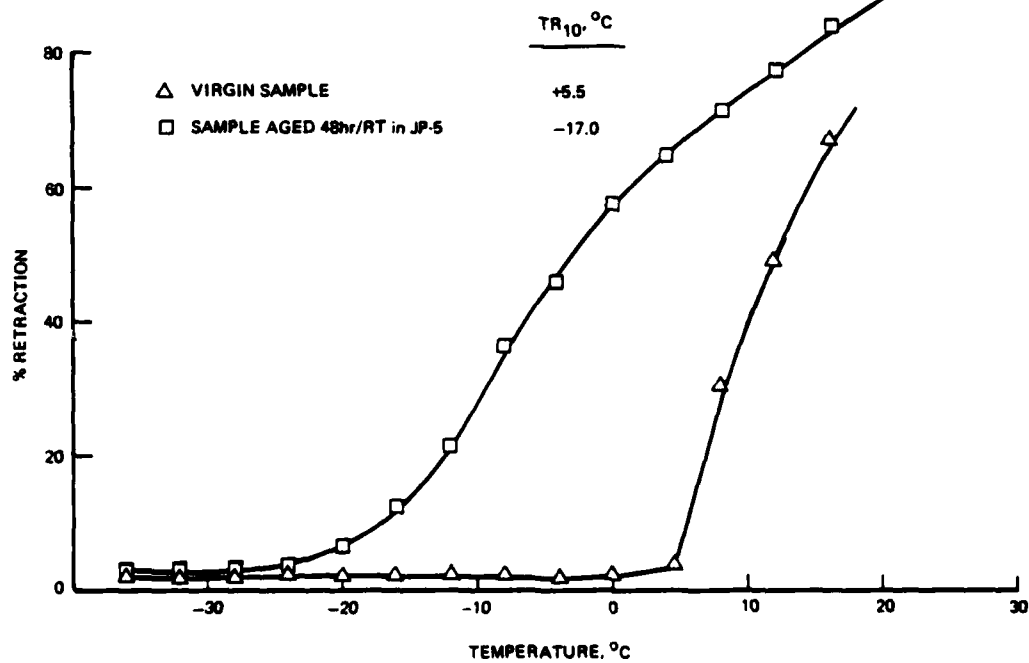


Figure 52. TR_{10} Curves for Aflas: EPDM Blend Containing Cab-O-Sil M5 Coated with 3-(heptafluoroisopropoxy) propyltrimethoxysilane

Table 47. Formulation of Aflas/EPDM Blend for Evaluation of Plasticizers

<u>Compound 14919-62-1</u>	<u>phr</u>
Aflas 100H	100
Norde1 1040	10
Carnauba Wax	1.5
Austin Black 325	10
Teflon T-8A	5
B-3000 Resin	5
Diak #7	3
Vulcup R Peroxide	2.5
	<u>137.0</u>

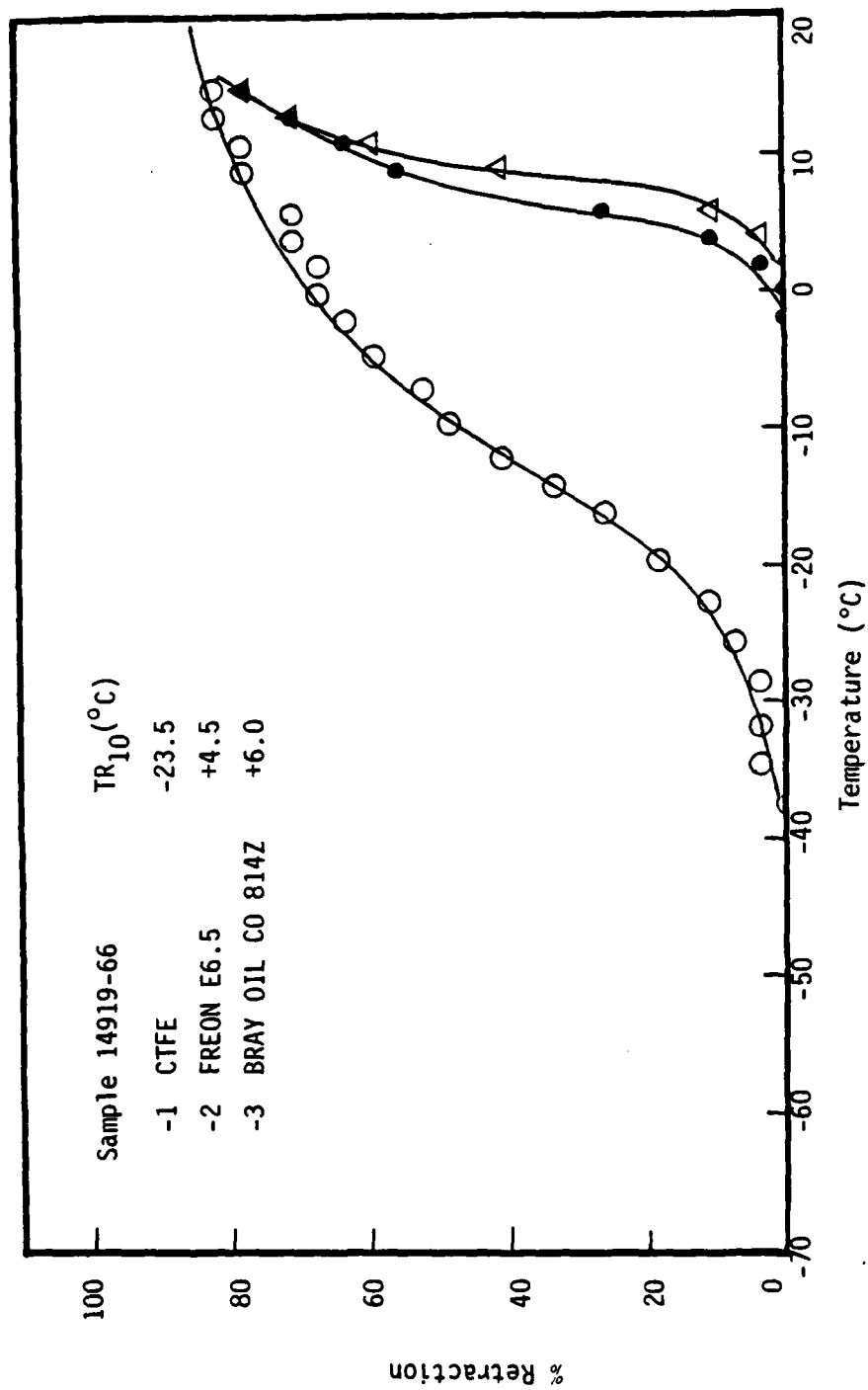
Cure: 30'/160°C (320°F)
Postcure: 8 hr/232°C (450°F)

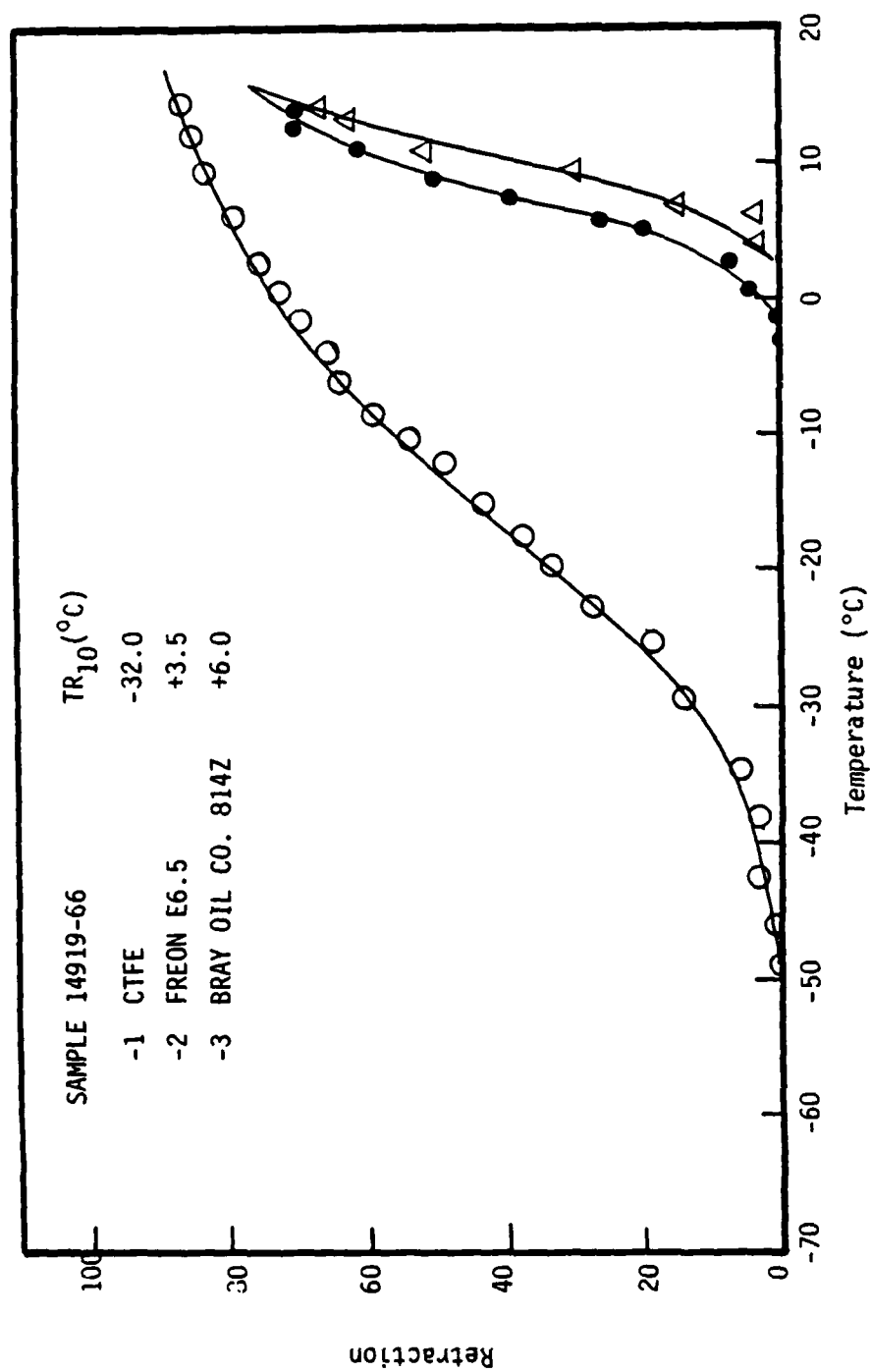
Samples were also swelled in CTFE for comparison. At the end of that time period, neither the Freon nor 814Z fluids had swelled the samples. For the first TR₁₀ test, the test tubes containing these fluids were placed in an oven for 2 hr/135°C (275°F), giving a volume swell of 3.6% for each. As the CTFE samples had swelled to 87.0%, these samples were dried 2 hr/100°C (212°F) in vacuo to reduce the volume swell to 40%. TR₁₀ tests were then run on the samples.

To insure that all samples were at equilibrium for the second TR₁₀ test, the Freon and 814Z samples were swelled 24 hr/135°C (275°F) following the 120 hr/RT soak. Resultant volume swell was still 3.6%. The TR₁₀ temperatures for each sample are as follows (curves are shown in Figures 53 and 54):

TR₁₀ Temperatures for Aflas:EPDM Blend Swelled in Various Fluids

Fluid	$\Delta V\%$ at test		TR ₁₀ (°C)	
	Test ₁	Test ₂	Test ₁	Test ₂
CTFE	40.5	39.9	-23.5	-32.0
Freon E6.5	3.6	3.6	+ 4.5	+ 3.5
Bray Oil Co. 814Z	3.6	0	+ 6.0	+ 6.0

Figure 53. TR_{10} Curves From Test 1.

Figure 54. TR_{10} Curves From Test 2

The only discrepancy is in the two results for the CTFE samples which differ by 9°C. The result from Test 2 is probably the more accurate of the two, as it had longer to equilibrate before testing. However, it is quite clear that neither Freon nor 814Z act as a plasticizer for this Aflas:EPDM compound.

The final fluid evaluated as a possible plasticizer for Aflas/EPDM blends was the vinyl-terminated fluorinated plasticizer (depicted earlier in Figure 45) that Dr. Kirby Scherer of USC synthesized. The underlying theory was to graft the plasticizer onto the polymer backbone, thus preventing extraction. A recent paper presented by R. J. Eldred of General Research Laboratories suggests that grafted plasticizers can be effective⁽¹⁷⁾.

The initial evaluation of Dr. Scherer's plasticizer (designated FP) was conducted with compound 15145-6-1 described in Table 48. Upon curing, the compound blistered and could not be tested further. A thermogravimetric analysis (TGA) was conducted on the plasticizer under nitrogen flow to determine its volatility (weight loss) as a function of temperature. As Figure 55 indicates, FP is volatile at low temperature, and thus cannot immediately be exposed to the temperatures the Aflas/EPDM compound requires to cure.

For the second study, a two-step cure was performed using compound 14808-65-1 listed in Table 48. For the first step--to graft the plasticizer onto the polymer backbone -- all ingredients, except for the Vulcup R peroxide, were combined. The compound was heated 20', 177°C (260°F). Extraction of samples of the compound with isopropyl alcohol before and after heating was performed to ensure the plasticizer had completely reacted; following heating, no material was extracted over 6.5 hours immersion in IPA. Vulcup R peroxide was then added, followed by conventional curing of the compound in a mold.

A TR₁₀ test was next conducted (Figure 56), which showed the compound to have a TR₁₀ value of 4.0°C, the same as that of the base polymer. Therefore, this chemical also does not act as a plasticizer for Aflas/EPDM.

TRW postulates that the bulky chlorine atom present in CTFE is responsible for its plasticizing action. This may be why the structures evaluated under this program - in particular the vinyl terminated plasticizer

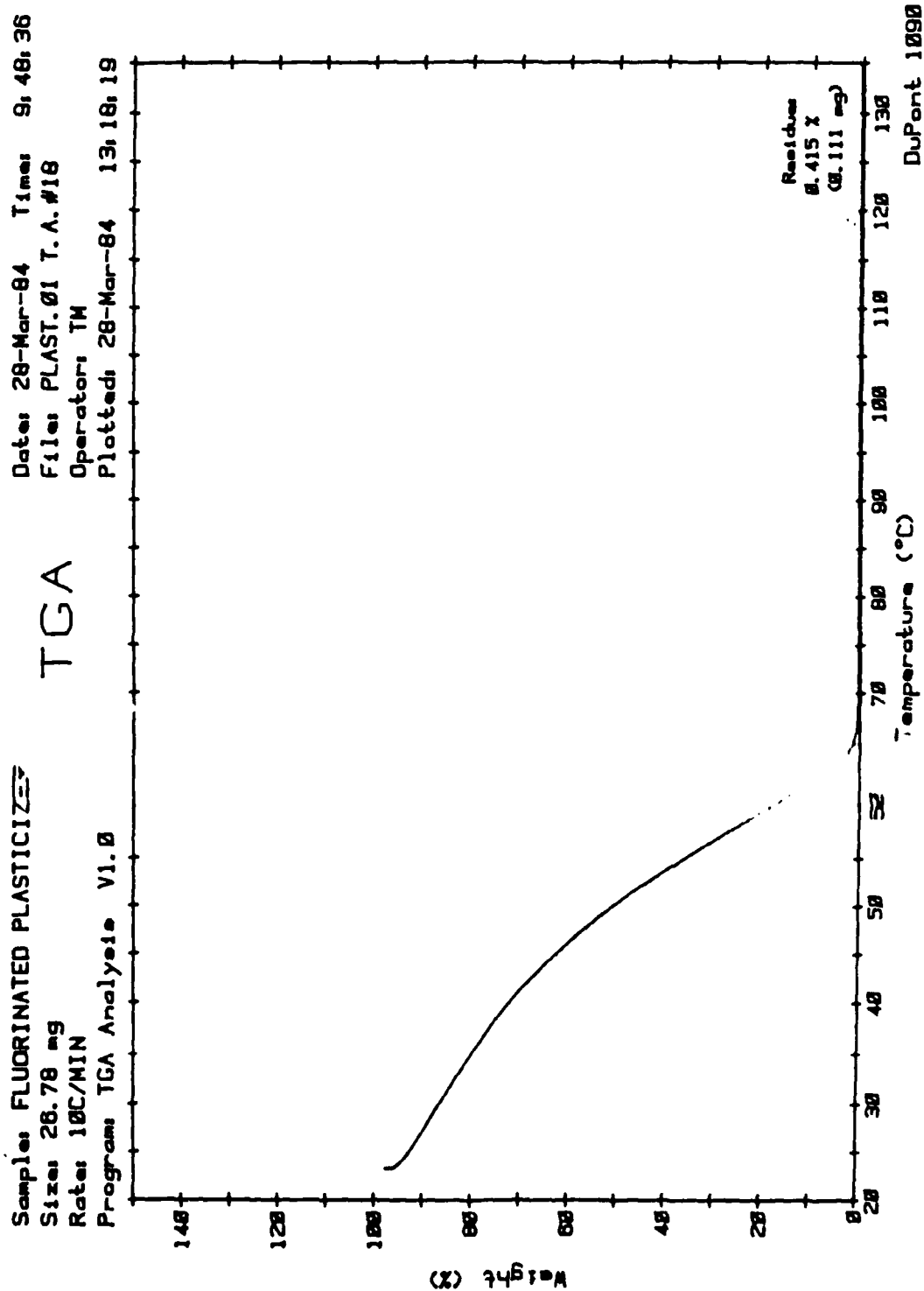


Figure 55. TGA Curve of Vinyl Terminated Fluorinated Plasticizer Synthesized by Dr. Scherer of USC

Table 48. Evaluation of Vinyl-Terminated Fluorinated Plasticizer (FP) Synthesized by Dr. Scherer

<u>Compound</u>	<u>15145-6-1</u>	<u>14808-65-1</u>
Aflas 100H	100	100
Nordel 1040	15	15
Carnauba Wax	1.5	1.5
Cab-O-Sil M5	20	20
FP	10	10
Diak #7	1.5	1.5
Vulcup R Peroxide	2.5	2.5
Benzoyl Peroxide	--	1.5
Preheat Before Cure:	N/A	20'/127°C (260°F)*
Cure:	30'/160°C (320°F)	30'/160°C (320°F)
Postcure:	8 hr/232°C (450°F)	8 hr/232°C (450°F)

*Prior to Vulcup R addition

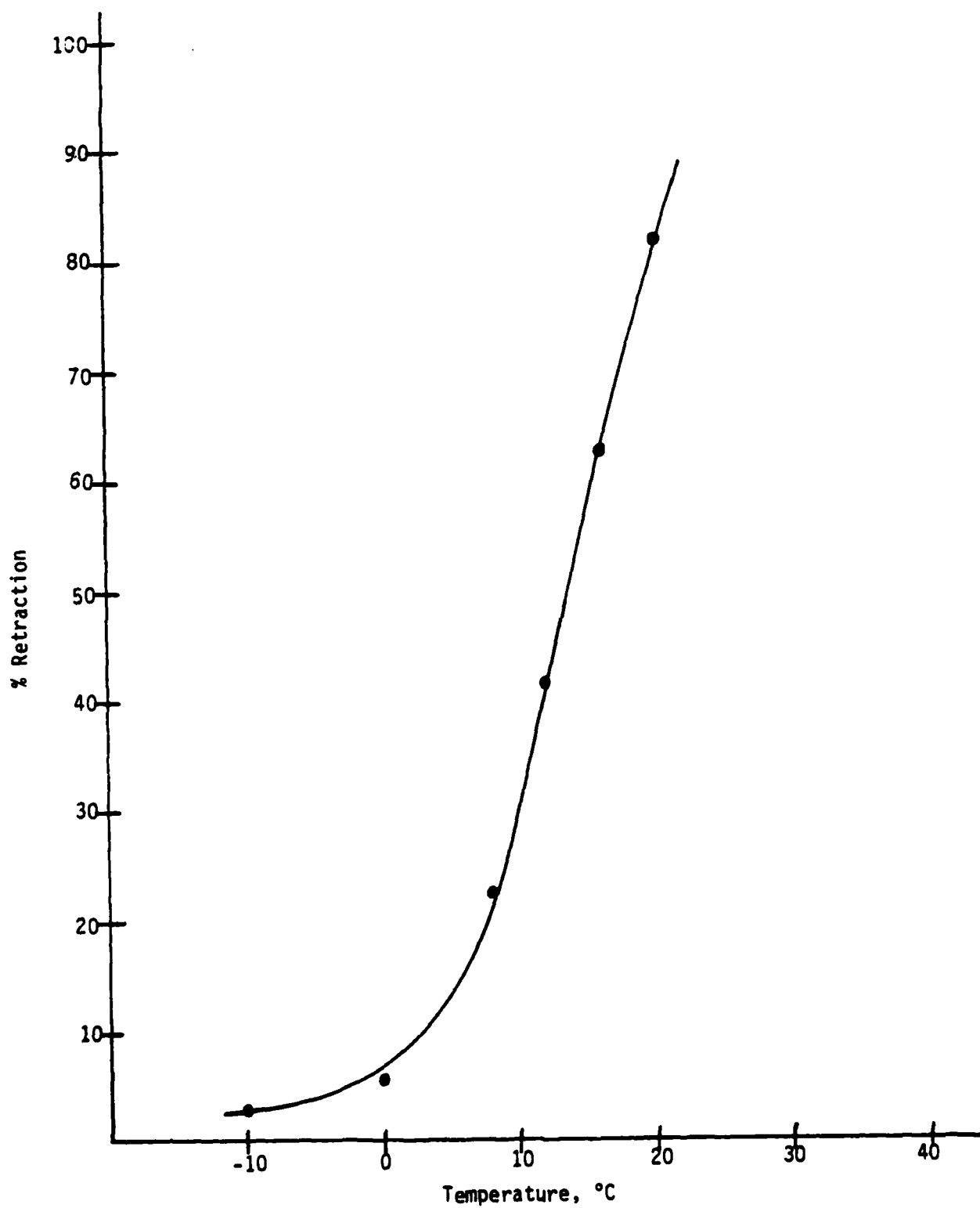


Figure 56. TR_{10} Curve for FP Plasticizer Grafted on Aflas:EPDM Compound

synthesized at USC - did not provide the anticipated results. Thus, further exploration into synthesis of vinyl-terminated CTFE is needed to determine if this postulate is correct.

6.0 MATERIALS COMPATIBILITY CONCLUSIONS

In keeping with the two objectives of the materials compatibility task, this section is divided into two parts:

- o Conclusions regarding nitrile studies
- o Conclusions regarding alternative polymer systems for nitriles

All conclusions are based on a nitrile compound conforming to specification MIL-P-83461 (Table 1) as the control compound throughout this program.

6.1 NITRILE STUDIES: CONCLUSIONS

1. The approach of stabilizing conventional nitrile rubber compounds by adding small amounts of an identified peroxide decomposer, manganese dioxide (MnO_2), is not effective. Samples containing MnO_2 showed similar degradation to those without MnO_2 when aged under identical conditions.

2. Adding MnO_2 directly to JP-5 to inhibit peroxide attack is also ineffective.

3. A study conducted with nitrile:EPDM blends exposed to JP-5 containing peroxides indicates the Navy can improve performance of nitrile seals by using nitrile polymers with higher acrylonitrile contents than are currently used. This would reduce the amount of unsaturation in the polymer backbone. (MIL-P-83461 compound is based on a nitrile polymer with an acrylonitrile content of 27 mole-%.)

4. To achieve the best resistance to degradation caused by aromatics in JP-5 fuel, nitrile polymers with an acrylonitrile content of 40 mole-% should be used. (This is consistent with #3, indicating the Navy can immediately increase a seal's lifetime by changing the base polymer from Krynac 27.50 to Krynac 40.65.)

5. The ability of conventional nitrile compounds (such as those conforming to MIL-P-83461) to withstand degradation caused by aromatics in the fuel is independent of the concentration of aromatics between 5% and 25% w/w.
6. A mixed sulfur/peroxide cure system in nitrile compounds does not appear to be more resistant to degradation caused by JP-5 containing peroxide than peroxide-cured nitrile compounds.
7. Because of a different cure system requirement, Nippon Zeon's highly saturated nitriles (Zetpol polymers) cannot be used as "drop-in" substitutes for conventional nitriles; however, initial tests indicate that formulations based on Zetpol polymers will offer better resistance to JP-5, containing peroxide than conventional unsaturated nitrile polymers.
8. Di-t-butyl peroxide is not a good "referee" for naturally "grown" peroxides in JP-5 as conventional nitriles are stable to the former but not to the latter.
9. The presence of an antioxidant(s) in JP-5 inhibits the growth of peroxides in the fuel. Powerine JP-5 (NFP-1) contains an antioxidant(s), limiting the growth of peroxide at 100°C (212°F) to 0.8 meq/l (6.5 ppm). In contrast, Exxon JP-5 (NFP-2) without any antioxidants, experienced peroxide growth of over 156 meq/l (1248 ppm) at 71°C (160°F).

6.2 ALTERNATIVE POLYMER SYSTEMS: CONCLUSIONS

1. Firestone's PNF-280-009 is stable in JP-5 containing high levels of peroxide; however, because of relatively poor original tensile properties, PNF is only recommended as an alternative to static nitrile seals currently used.
2. An Aflas/EPDM/Chlorotrifluoroethylene (CTFE) terblend developed under Air Force Contract F33615-82-C-5021 is also stable in JP-5 containing high levels of peroxide. However, JP-5 extracts at least 85% of the CTFE present in the blend, and causes the blend to excessively swell (>20% v/v).

3. JP-5 is a partial plasticizer for Aflas/EPDM blends; however, it is not as effective as CTFE.

4. The following solvents are ineffective plasticizers for Aflas/EPDM blends:

- o Sunpar 2280 (paraffinic oil)
- o Kel-F 800 (high molecular weight CTFE)
- o 3-(heptafluoroisopropoxy)-propyl trichlorosilane
- o 3-(heptafluoroisopropoxy)-propyl trimethoxysilane
- o Bray Oil 814Z
- o Freon E6.5

5. A vinyl terminated fluorinated plasticizer synthesized at USC also does not plasticize Aflas/EPDM when grafted onto the polymer backbone. TRW postulates that the bulky chlorine group present in CTFE gives CTFE its plasticizing ability. Thus, a vinyl-terminated CTFE solvent may prove to be an effective non-extractable plasticizer.

6. To counteract the problem of excessive swell of Aflas/EPDM blends in JP-5, a seal can be molded undersized, then swelled to size in JP-5 for use. The resultant swelled blend meets the requirements set down by the Air Force and MIL-P-83461 for seal compounds used in hydraulic systems.

7.0 MATERIALS COMPATIBILITY RECOMMENDATIONS

As outlined in the conclusions section, there are two relatively easy options the Navy can immediately implement to increase a nitrile seal's performance.

1. Specify nitrile polymers with an acrylonitrile (ACN) content of 40 mole-% (such as Krynac 40.65). Based on the results of several experiments, this level appears optimum. The percent unsaturation in the polymer backbone is thereby reduced, and as it is this backbone unsaturation which is the site of peroxide or aromatic attack, this change would reduce the amount of sites available for attack. (MIL-P-83461 currently specifies nitrile polymers with an ACN content of 27 mole-%).

2. Require suppliers of JP-5 to include an antioxidant(s) in the fuel such as Powerine JP-5 (NFP-1). The antioxidant inhibits peroxide growth in the fuel.

The above are short-term solutions; however, because conventional nitriles have unsaturated backbones, they will always be susceptible to peroxide or aromatic attack, leading to degradation of the seal.

A longer-term solution is to change to an alternative polymer system. This program indicated two polymer systems that could provide the Navy with seals that are more stable to peroxide attack; however, further work is needed to optimize them.

The most promising of the two are the new highly saturated nitrile polymers (Zetpol) produced by Nippon Zeon. Initial testing indicated these polymers are more stable than conventional nitrile polymers as they have relatively little backbone unsaturation. Testing would involve JP-5 containing high levels of naturally "grown" peroxides.

A second approach is to further explore the synthesis of vinyl-terminated CTFE as a plasticizer for Aflas/EPDM blends. The blend offers additional advantages, as it is stable to 316°C (600°F) and also contains no backbone unsaturation.

If it is the Navy's desire to continue using nitrile seals, further work can also be conducted in the area of developing additional inputs for a specification that could be used to characterize JP-5 fuel. Specifically, there are three areas for future studies:

1. Nitrile degradation is independent of aromatic concentration between 5 and 25% w/w. A study is needed to determine the effect of aromatic concentration between 0 and 5% w/w. It may be that 5% w/w is a critical concentration resulting in zero order kinetics. The Navy could then specify 5% as a limit on aromatic content of JP-5.
2. Di-t-butyl peroxide proved to be an ineffective referee for peroxides naturally "grown" in JP-5. If such a referee could be found, a possible quality control specification could be devised for qualifying seal compounds. Various peroxides would be selected for addition to JP-5. Degradation of MIL-P-83461 compounds in this referee fluid could be compared with degradation of an identical compound in JP-5 containing "grown" peroxides.
3. Despite efforts to "grow" peroxides in NFP-14 identical to the procedure used for successfully "growing" peroxides in NFP-2, a peroxide level greater than 5 meq/l (40 ppm) could not be reached. A detailed analysis of NFP-14 would indicate what leads to its effective resistance to peroxide growth. In all probability, NFP-14 contains an effective antioxidant the Navy could specify all suppliers must add to JP-5.

8.0 FUEL LUBRICITY

8.1 INTRODUCTION

The problem of low lubricity JP-5 fuels has been one of growing concern to the Navy over the past ten years. In general, the problem is believed to be caused by increased hydrotreating and clay filtering at the refinery level which tends to remove the polar compounds or surfactants that act as boundary lubricants. The result is a low lubricity jet fuel which may cause various problems, most notably scoring of main engine gear pumps operating in the boundary lubrication regime.

At present, the military specifications for JP-4 and JP-5 aviation turbine fuels (MIL-T-5624) does not contain a specification for fuel lubricity. Indeed, no clear cut standard exists for lubricity measurements and evaluation outside of large scale gear scoring tests, which are expensive and time consuming. As required by MIL-T-5624, corrosion inhibitors are added to JP-4 and JP-5 but no lubricity additives are required.

Since low lubricity JP-5 fuels can render Navy jet aircraft inoperable, it is desirable to develop an effective solution to the problem of lubricity. Essentially, this can consist either of a hardware modification to allow the use of low lubricity fuel or it can involve the use of an additive to ensure adequate fuel lubricity. HITEC E-515, a corrosion inhibitor qualified for military use, has been found to be effective in eliminating low lubricity problems and has been used on pacific fleet aircraft carriers⁽¹⁸⁾. However, the use of an additive is not without disadvantages. The fuel additive is expensive, it is a deterrent to the satisfactory operation of filter separators, and its initial use will release corrosion products from iron pipelines. Therefore, eliminating a problem of inadequate mechanical design with a fuel additive can produce other problems⁽¹⁹⁾.

Ideally, the optimum long term solution to the lubricity problems of jet fuel involves the modification of hardware to yield Navy aircraft which can perform adequately with any JP-5 which may be encountered. However, a major obstacle to this approach is the inadequacy of current fuel system qualification procedures as discussed briefly below.

The qualification procedure for fuel systems generally involves the use of harsh isooctane in a recirculating system to simulate a low lubricity fuel. Since harsh isooctane has a lubricity much lower than the JP-5 fuel which is causing problems in the field, the use of an additive such as HITEC E-515 in the jet fuel should not be required with qualified hardware provided the qualification procedure is adequate. However, the difficulty lies in the fact that the lubricity of isooctane can vary greatly and is known to improve during recirculation through fuel system components. Therefore, it is possible that the isooctane used for qualification testing may have exceptional lubricity depending on its history; and, thus, a fuel system which qualifies with isooctane may fail in the field while running with jet fuel.

What is needed is a device which can quickly and effectively measure lubricity to permit frequent monitoring of the test loop condition to ensure that tests are performed with known and sufficiently harsh isooctane. Obviously, such a device would also be an invaluable tool in research as well as in the evaluation of various additives. TRW/Lucas Dwell Tester is believed to be such a device.

8.2 OBJECTIVES

The objectives of this program are to investigate the role of additives and sulfur compounds in lubrication and to evaluate the usefulness of the TRW/Lucas Dwell Tester in determining fuel lubricity.

To accomplish these objectives, Lucas and BOCM tests were performed on various fuels to provide a comparison between the two devices. In addition, Lucas tests were run on fuels spiked with different corrosion inhibitors qualified for use in JP-4 and JP-5. A list of these additives is given in Table 49. In a similar manner, fuels spiked with sulfur compounds typically found in JP-4 and JP-5 were tested for lubricity using the Lucas device.

8.3 BACKGROUND

8.3.1 Relationship of Gear Tooth Scoring and Boundary Friction

Current theories on gear tooth scoring have indicated that two different criteria exist for predicting scoring with spur gears. For elastohydrodynamic lubrication films, the minimum film thickness concept reportably provides

TABLE 49. QUALIFIED ANTICORROSION ADDITIVES (27)

<u>Additive Name</u>	<u>Manufacturer</u>	<u>Min Effective Conc (ppm)</u>	<u>Max Effective Conc (ppm)</u>
HITEC E-515	Edwin Cooper, Incorporated	24.5	52.3
HITEC E-580		9.4	25.1
DCI-4A	E.I. duPont de Nemours & Company	9.1	24.3
DCI-6A		9.1	24.3
NALCO 5403	Nalco Chemical Company	9.2	24.5
NALCO 5405		9.2	24.5
TOLAD T-245	Petrolite Corporation, Tretolite Division	22.4	35.9
TOLAD T-249			
UNICOR-J	UOP Processes Division	9.2	24.5
Lubrizol 541	Lubrizol Corporation	8.9	17.8
MOBILAD F-800	Mobil Chemical Company	9.9	26.5
ARCO 4410	ARCO Performance Chemicals Corporation	9.0	24.0

reliable scoring predictions, while in the boundary lubrication regime, the critical or flash temperature concept is the most reliable method⁽²⁰⁾. Since aircraft fuel pumps typically operate in the boundary lubrication regime, the flash temperature concept as originally defined by Blok⁽²¹⁾ is the preferred method. The usefulness of the flash temperature concept has been further confirmed by over ten years of experience at TRW with a variety of aircraft fuel pump models.

The background for the TRW methodology is as follows: Following Blok, we define a flash temperature, the highest temperature experienced by contacting metal surfaces, as T_f . T_f is equal to T_1 , the bulk temperature, plus T_2 the instantaneous surface temperature. T_2 is related to properties of the gear material, the velocity, the load distribution and, most importantly, the coefficient of friction in the gear tooth contact zone. With Blok's formulation, to be given below, a measurement of the coefficient of friction allows us to calculate T_2 under given conditions and thus to determine T_f . Once the scoring threshold value of T_f is known, then gear tooth scoring can be predicted on the basis of the boundary friction coefficient, f , and a measure for f for different fuels provides a realistic evaluation of the lubricity of the fuel with respect to the gear tooth scoring phenomenon.

The Blok formulation for two meshing gears of identical material is

$$T_2 = \frac{C \cdot f \cdot W_n}{\sqrt{b/2}} \left| \sqrt{V_1} - \sqrt{V_2} \right|$$

where:

- C Material constant including specific heat, thermal conductivity and density. Also included are surface finish effects and a temperature distribution factor.
- f Coefficient of friction in the gear tooth contact zone.
- W_n Normal tooth contact load per unit effective gear face width.
- b Instantaneous width of elastic tooth contact zone, based on gear tooth flank curvatures at idealized contact point.
- V_1, V_2 Instantaneous rotational gear tooth flank surface velocities at idealized contact point.

The experimental work conducted over the past four years at TRW has shown that the relationship between measured friction factors and gear scoring as discussed above does exist. Obviously, a prerequisite for this work was to devise a suitable method for the measurement of boundary friction. Such a method is described in the following paragraphs.

8.3.2 Lucas Dwell Tester

Because of its ready availability in our laboratory and its widely adjustable operating range, the Lucas Dwell Tester was selected as the apparatus for friction measurement. This device uses a stylus on a vertical shaft mounted, rotating disk for the measurement of frictional forces. The stylus is mounted on a beam type load arm, which is free to deflect under the influence of the frictional drag force. The load arm in turn is connected to a linear variable differential transformer for conversion of the beam deflection in the horizontal direction into a proportional electrical signal, which is then amplified and recorded on a strip chart. Typically, the resulting traces reveal a characteristic oscillation pattern with an amplitude of lesser magnitude than the average signal (See Reference 22 for a discussion on the cause of these oscillations.) The average frictional drag force is visually estimated by drawing a line through the recorder trace at the mean level, similar to a center of gravity estimate. The corresponding friction coefficient is calculated as the ratio of the average drag force divided by the total stylus load as shown below:

$$f = \frac{F}{W}$$

where:

f = friction coefficient

F = frictional drag force parallel to V

W = normal force or total stylus load

The performance of this machine was originally less than satisfactory with the initial lubricity test method as specified by Lucas. However, TRW has made the following changes in the test methods and hardware to obtain accurate and repeatable results:

- o The device is operated with a flooded disk. This condition is maintained throughout the measurement by constant replenishment of the test fluid which minimizes concentration of boundary lubricants by test fluid evaporation.
- o To assure operation in the boundary lubrication regime, the rotational shaft speed was reduced to 25 rpm and the stylus diameter was decreased to 0.7 mm. These changes were made because it has been demonstrated that at the originally specified shaft speed the larger stylus can generate significant hydrodynamic load capacity when operated in a flooded condition. This effect depends on test fluid viscosity and is a distorting influence in the measurement of boundary friction.
- o The original non-ferrous stylus material was changed to mild M1020 steel. This increased the dry friction coefficient to more closely approach that of the gear material.

Figure 57 is a photograph of the TRW modified Lucas Dwell Tester.

The friction measurements obtained by this revised approach has been very repeatable with a precision of approximately 5%. In addition, the machine has demonstrated an extreme sensitivity to the presence of anticorrosion additives as discussed in Sections 8.4.3 - 8.4.7

8.3.3 Experimental Procedure

The following presents details regarding the use of the TRW/Lucas Tester.

8.3.3.1 Disk Preparation

Experience has shown that acceptable friction measurements can only be achieved with a polished disk test surface. Even relatively small pits and scratches can have a detrimental effect on the drag force measurement. It is suspected that boundary lubricants, attached to these surface imperfections,

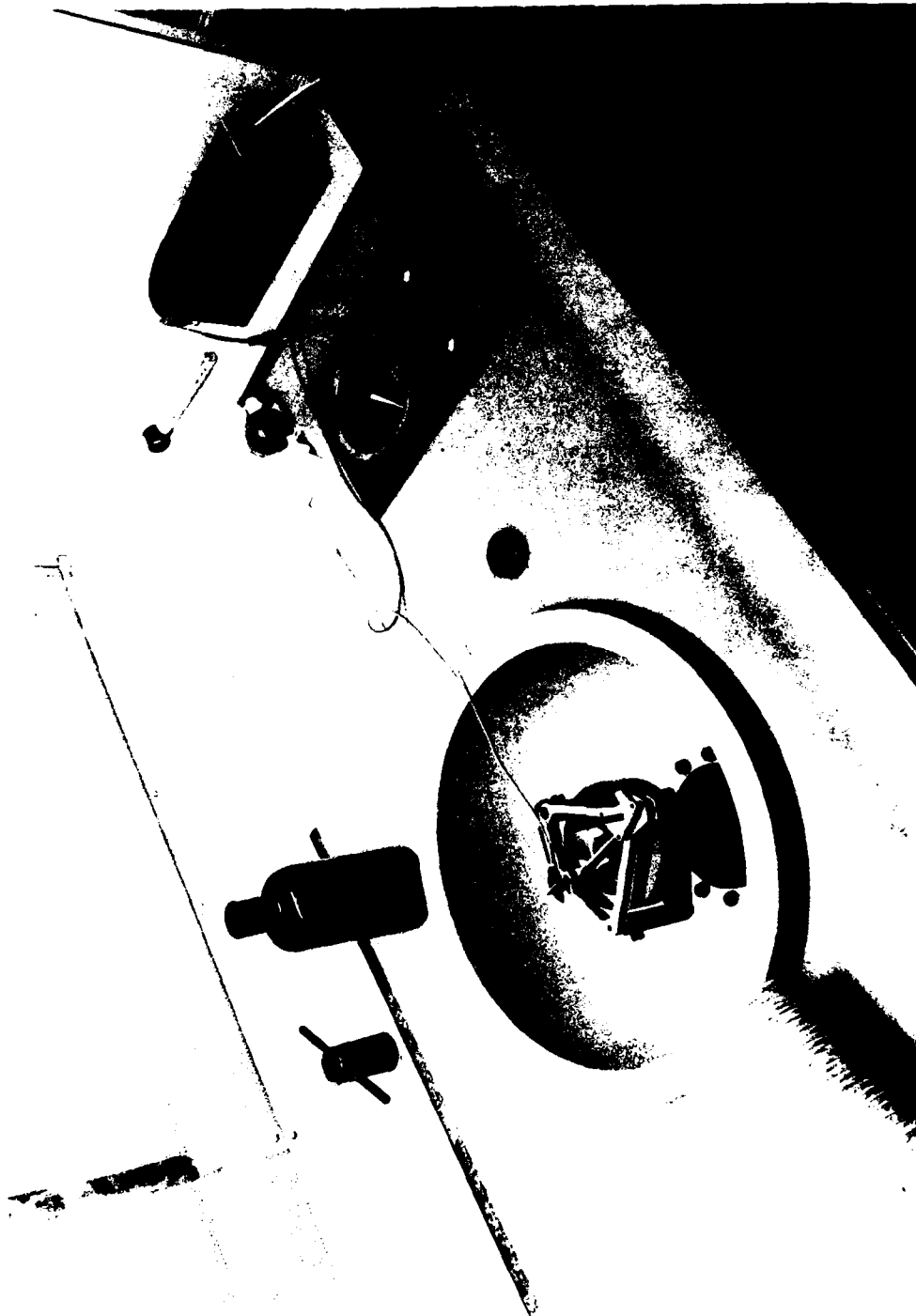


Figure 57. Lucas Dwell Tester as Modified by TRW for the Measurement of Fuel Lubricity by the Friction Factor Method

cannot be readily removed by the cleaning process and are gradually released during subsequent lubricity measurement, resulting in erratic or unrealistically low friction forces.

Prior to each day's tests, the Lucas disk is examined for surface blemishes and is reconditioned as necessary. If complete reconditioning of the test surface is needed, surface grinding is used to remove all undesirable features. The material removal is performed in small incremental steps to avoid local overheating and grinding chatter. All vestiges of grinding marks have to be subsequently removed by lapping followed by machine polishing. The machine polishing is accomplished first with a six micron and then a one micron diamond polishing compound, each step followed by a thorough cleaning of the disk with acetone using a soft paper towel. In the event that only minor reconditioning of the disk is needed, then the machine grinding and lapping steps are deleted.

The final step in disk preparation is the cleaning procedure. This procedure is always performed immediately prior to testing and involves the following steps. First, a thorough washing of the entire disk is performed using an acetone sponge andalconox detergent is diluted in water to 1 part in 100. The disk is then rinsed with deionized water and blown dry with a high purity nitrogen gas. Next, the disk is placed in an ultrasonic cleaner after which the disk is installed on the Dwell Tester spindle. Activated charcoal powder is applied to a small section of a folded, soft, contaminant free paper towel and the towel is applied with finger pressure to the disk rotating at 500 rpm. After uniform drag has been achieved and the disk can be slowed down to 100 rpm by finger pressure on the towel, the test surface is ready for initial break-in with harsh isooctane as discussed in Section 8.3.3.3.

8.3.3.2 Stylus Preparation

The small stylus diameter and the requirements for close conformity between disk and stylus test surfaces makes separate stylus conditioning, analogous to the disk preparation, impractical if not impossible. Instead, a pre-test stylus break-in, as described in the Section below, using the test disk and harsh isooctane ($f = 0.5$), has been found to be expedient and effective.

8.3.3.3 Test Method

In order to minimize the possibility of accidental test equipment contamination, the friction measurements are performed in a completely enclosed area, reserved for only this purpose, which is constantly supplied with a forced flow of filtered air. The filtered air flow rate is of sufficient magnitude to maintain a slight atmospheric overpressure in the test area, so that the intrusion of airborne contaminants may be kept to a minimum. A flexible forced exhaust line with a movable inlet, which can be placed in close proximity to the work station, is used for the removal of toxic test fluid vapors.

During the friction measurements the test fluid is applied at an even rate to the disk test surface with the aid of a pipette. This method of application was chosen because a pipette can be fairly easily cleaned or, if excessively contaminated, simply discarded without great expense. The rate of fluid replenishment is kept well above the fluid evaporation rate, resulting in an overflow, so that evaporative concentration of boundary lubricants above the prevailing specimen levels will be avoided, or at least minimized.

Each day's testing is preceded by a calibration of the friction force measuring system. With the load frame mounted in a special calibration fixture, at 90° relative to its normal attitude, various weights, ranging from 10 gram to 50 gram in 10 gram increments, are suspended from the stylus and the readout is recorded. Adjustments, if necessary, are made at this time.

Individual tests are preceded by preparation of the disk test surface as outlined in Section 8.3.3.1, followed by a test surface break-in with harsh, clay filtered isooctane with a known boundary friction coefficient of at least 0.5. The disk and stylus test surface break-in is performed with a supplemental load of 80 gram at a rotational disk speed of 25 rpm, until the stylus drag force uniformly exceeds the recorder limit of 50 gram. At this point the supplementary weight is reduced to 30 gram and the break-in run is continued until the measured drag force has stabilized at a steady average value. If this friction coefficient duplicates, or is close to the previously established value for the break-in fluid, the unit is ready for testing of the actual fluid specimen, which shall commence immediately to minimize the possibility of test equipment re-contamination. Otherwise the surface

break-in has to be continued, or in stubborn cases the entire conditioning procedure may have to be repeated.

Testing of the fuel sample is performed at a rotational disk speed of 25 rpm with at least four stylus load settings, favoring the high end of the attainable load range. The corresponding friction coefficients are calculated and their arithmetic average is reported as the representative value. The empirical acceptance criteris for test validity is that at least 75% of the original friction coefficients have to fall within +5% of the arithmetic average. Past experience has shown that the measurement accuracy is considerably enhanced by the practice of averaging.

8.3.3.4 Fuel Samples

As previously mentioned, the lubricity of a fuel sample can be significantly increased by minute amounts of contamination. Such contamination can occur at any time from the moment the sample is drawn until the lubricity evaluation is completed. Therefore, careful attention was paid to cleaning of sample containers as well as transferring of fuels and handling during testing.

With the exception of isooctane, all fuel samples used in this program were stored at TRW, Space Park (Redondo Beach, CA.) in one gallon jug bottles which had been sparged with nitrogen. Originally, the fuel samples designated NFP-2 and NFP-3 were stored in a refrigerator maintained at approximately 10°F. However, this practice was terminated after about six months when it was found the fuel friction values were undergoing a slight change. Subsequent to that time, all fuel samples were stored at room temperature.

In those cases where isooctane was used as a test fuel, the samples were taken directly from 55 gallon drums at TRW, Cleveland, on an as needed basis. To ensure fuel harshness, the fuel samples were passed through a Gamah rig just prior to additive addition and testing at Cleveland.

Since most of the fuel samples were stored over 2000 miles from the site of lubricity testing, it was necessary to use sample containers approved by the D.O.T. for shipment. The requirements of DOT 49CFR have been found to be met using a composite shipping kit marketed by Labelmaster under the Catalog Number KTF1662. Each shipping kit contains a one pint screw top bottle with

closure, a moulded DOT 33A protective foam pack and a 200 lb RSC shipping container. Unfortunately, the supplied bottle closure, which is equipped with a cone-shaped moulded polyethylene seal, will contaminate the fluid sample. However, the problem has been corrected by substitution of an aluminum foil lined bottle cap purchased from Arthur H. Thomas Co.

Cleaning of the sample containers prior to use involves the following steps. The bottle is filled with a high strength ALCONOX laboratory detergent and hot tap water solution and, after closure replacement, permitted to soak for at least ten minutes. Soaking is followed by vigorous scrubbing of all bottle and closure surfaces with a suitable brush, after which the detergent solution is discarded. Then the bottle and closure are repeatedly rinsed with hot tap water, accompanied by vigorous shaking, until the last tendency toward foam formation has completely disappeared. Subsequent to rinsing, the closure and interior bottle surfaces are generously wetted with undiluted LIQUI-NOX liquid laboratory detergent (ALCONOX-INC.) and, after closure replacement, permitted to soak for at least ten minutes. Then hot tap water is added and the scrubbing and rinsing procedure described above is repeated, except that two additional rinse cycles after complete disappearance of all foam vestiges are performed. After the final rinse, the bottle and closure are separately oven dried at 230° to 240°F. After cooling, the closure is replaced to minimize the risk of accidental container contamination.

Prior to drawing the fuel sample the bottle is conditioned by twice filling it partially full with fuel, replacing the stopper, and shaking vigorously followed by discarding the sample. Next, the bottle is thoroughly sparged with nitrogen gas for at least two minutes. At this point, the sample and additives if any are transferred to the pint bottle and sparged with nitrogen prior to sealing. The sample is then ready for shipment (if applicable) and subsequent testing.

8.4 DISCUSSION/TEST RESULTS

8.4.1 Evaluation of Test Parameters

During the initial testing of two JP-5 fuels labeled NFP-2 and NFP-3, it was found that neither the Lucas Tester nor the BOCM yielded repeatable results on samples drawn at different times. As seen in Table 50 and Figure 58, the friction factor values for each fuel appear to be getting milder with time and at about the same rate. This result was unexpected since the fuel samples were stored in refrigeration (10°F) prior to testing and thus would not be expected to undergo any chemical changes such as oxidation. Two possibilities appear likely; either the fuel samples were changing slightly with time, or certain variables involving the fuel handling procedures were not being adequately controlled. To evaluate these possibilities and to insure valid data, tests were performed to assess the adequacy of the fuel handling procedures and to determine the effects of refrigeration.

Table 50. Test Results on NFP-2 and NFP-3 for the Lucas Tester and BOCM

<u>Sample Number</u>	<u>Date Drawn</u>	<u>Date Tested</u>	<u>Fuel Designation</u>	<u>TRW/Lucas Friction Factor</u>	<u>BOCM Wear SCAR (MM)</u>
1A	11/4/82	11/12/82	NFP-2	.234	-
1B			NFP-2	-	.58
2A	11/18/82	11/23/82	NFP-3	.177	-
2B			NFP-3	-	.31
3A	12/9/82	12/17/82	NFP-2	.212	-
3B			NFP-2	-	.67
4A	12/9/82	12/16/82	NFP-3	.167	-
4B			NFP-3	-	.32
5A	1/13/83	1/25/83	NFP-2	.198	-
6A	1/13/83	1/25/83	NFP-3	.144	-

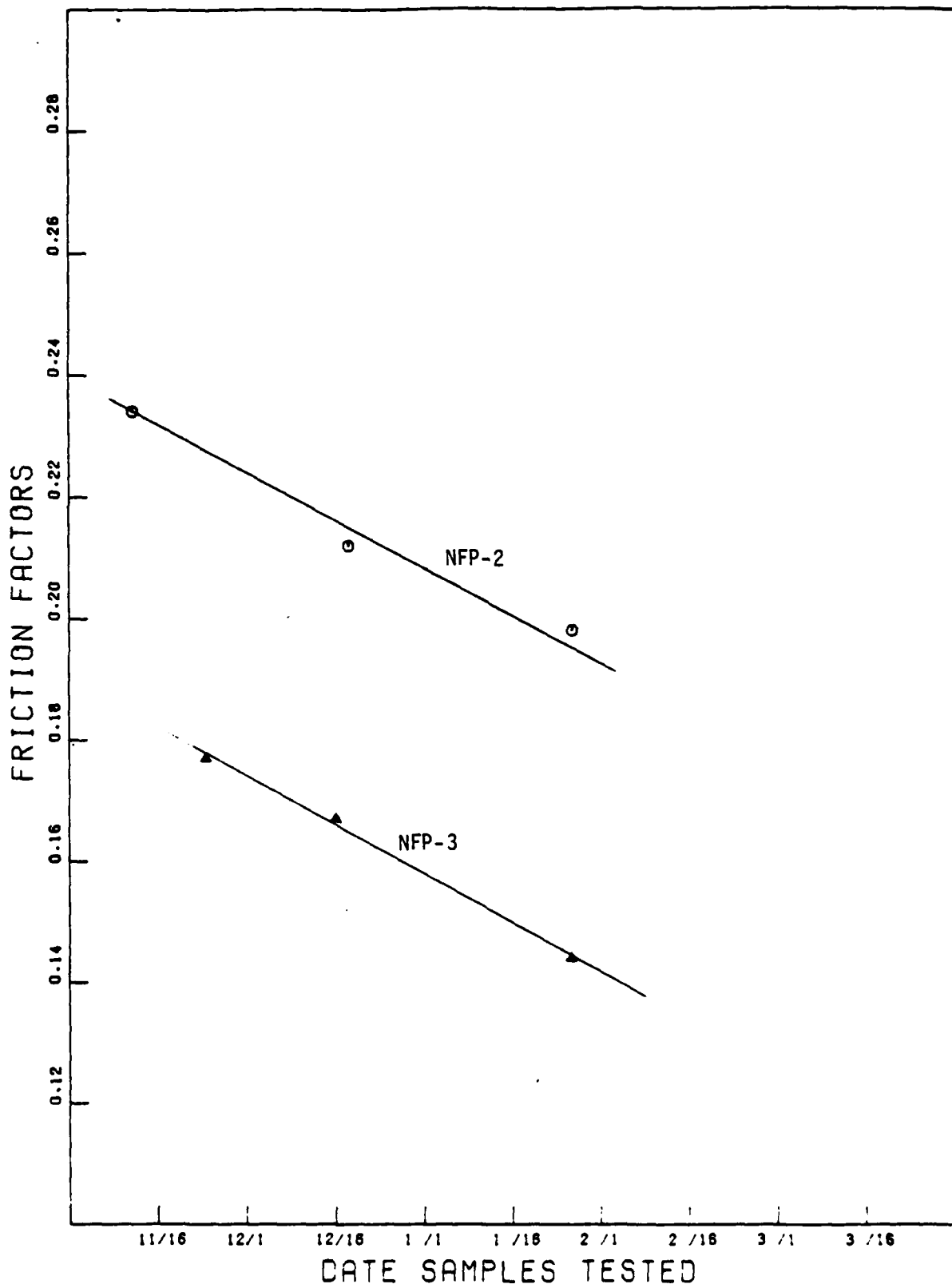


FIGURE 58.
TRW/LUCAS RESULTS FOR REFRIGERATED SAMPLES

Initially, the fuel samples were drawn from the gallon jug storage containers using a fuel transfer apparatus. This apparatus consisted of two rubber stoppers, one for the gallon jug and one for the pint bottle, connected by a stainless steel tube. The gallon jug was similarly connected to a nitrogen tank which was used to pressurize the jug and cause the fuel to transfer over to the pint bottle without exposure to air. The basic concern with the use of this apparatus was over the possibility of fuel contamination due to contact of the fuel with the stainless steel tube. In order to assess this possibility, three samples of NFP-3 were drawn on the same day using different transfer techniques. The first sample, labeled 21A, was drawn using the apparatus as described above while the other two samples were obtained simply by pouring the fuel from the jug into the pint bottles. Of these two, sample 22A was subsequently sparged with nitrogen while sample 23A was not. The results of the Lucas tests as seen in Table 51 show that the friction factors all agree within less than 4%. Sample 21A showed the lowest value with a friction factor of 0.155 while sample 23A yielded a friction factor of 0.161, the highest of the three samples. The conclusion drawn from these results is that the fuel is not picking up any significant contamination from the transfer apparatus. Furthermore, it was concluded that pouring is an

Table 51. Effects of Apparatus Transfer Methods on Friction Factors

<u>Sample Number</u>	<u>Date Drawn</u>	<u>Date Tested</u>	<u>Fuel Designation</u>	<u>TRW/Lucas Friction Factor</u>	<u>Sample Description</u>
21A	2/1	2/4	NFP-3	.155	Normal Transfer with Apparatus
22A	2/1	2/4	NFP-3	.156	Pour from Gallon Jug then N ₂ Sparge
23A	2/1	2/8	NFP-3	.161	Pour from Gallon Jug, No N ₂ Sparge

acceptable method of fuel transfer. All samples numbered higher than 21A were thus transferred by pouring.

Since it appears that fuel lubricity can change in refrigerated conditions it was decided to determine the effects of ambient temperature on the lubricity of previously refrigerated samples. This information is important since fuel samples sent from TRW, Space Park to Cleveland or Trenton are exposed to ambient conditions for varying periods of time prior to testing.

In the initial experiment, samples of NFP-3 were drawn and placed in ambient storage at periods of a week apart and then sent to Cleveland for testing, all at the same time. In all, three samples labeled 11A, 12A and 13A were shipped off on the same day the last sample (13A) was drawn. Table 52 contains the results of these tests while Figure 59 graphically presents the Lucas data as a plot of time out of the refrigerator versus the friction factor. In reviewing the data, it can be seen that sample 13A which was run on 2/16/83 at 8 days out of the refrigerator yielded a friction factor of 0.132. This data point is consistent with the expected value for an NFP-3 sample run in mid February based on Table 50 and Figure 58. However, samples 12A and 11A tested on 2/15/83 each showed higher friction factors than sample 13A with the values being progressively larger from sample to sample with increased time out of the refrigerator. Sample 11A, the first of the three samples drawn, showed the highest value with a friction factor of 0.162 at 23 days of ambient temperature. It should be noted that this value is close to the original NFP-3 value obtained in mid November of 1982. Thus, the Lucas data as discussed up to this point indicates that NFP-3 shows a decrease in friction factor due to refrigeration but regains its harshness with time at room temperature.

In order to verify the observed trends in the fuel behavior as seen with NFP-3 and as discussed above, a second experiment of the time/temperature tests were performed but this time with NFP-2. As before, one sample was drawn each week and placed in ambient storage until a total of three samples were collected. Unlike the results of NFP-3, the data for NFP-2 does not show a linearly increasing plot of friction factors with time out of the

Table 52.
Results of Time and Exposure to Ambient Temperature on Friction Factors

<u>Sample Number</u>	<u>Date Drawn</u>	<u>Date Tested</u>	<u>Fuel Designation</u>	<u>TRW/Lucas Friction Factors</u>	<u>BOCM Wear SCAR (MM)</u>
11A	1/25	2/15	NFP-3	.162	—
12A	2/1	2/15	NFP-3	.147	—
13A	2/8	2/16	NFP-3	.132	—
14A	1/25	2/24	NFP-3	—	.32
15A	2/1	2/22	NFP-3	—	.29
16A	2/8	2/24	NFP-3	—	.30
41A	2/18	3/16	NFP-2	.163	—
42A	2/25	3/30	NFP-2	.174	—
43A	3/4	3/16	NFP-2	.167	—

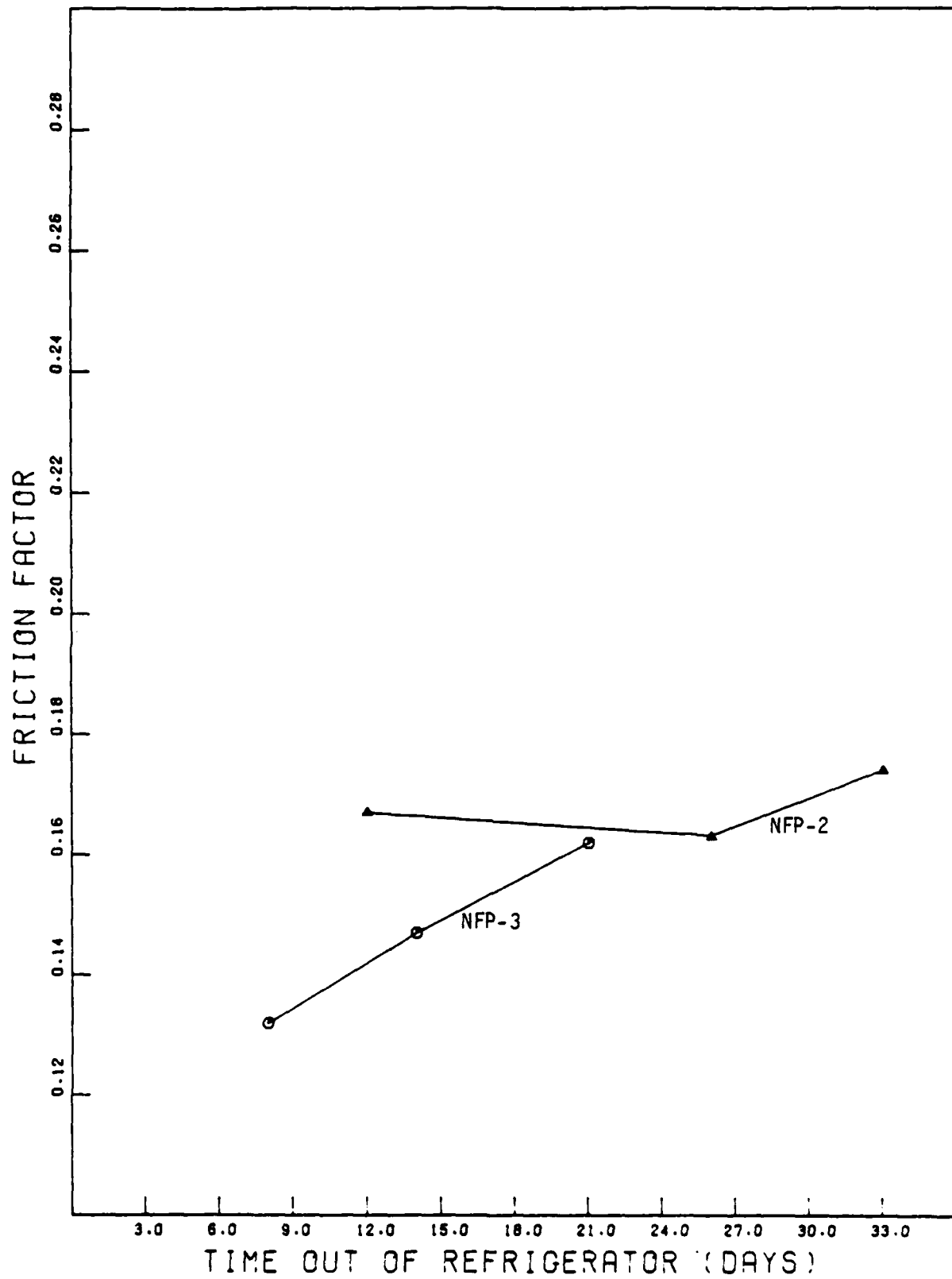


FIGURE 59.

TRW/LUCAS RESULTS FOR TIME/AMBIENT TEMPERATURE TESTS

refrigerator. Rather, the friction values stay relatively constant up to 26 days out of the refrigerator after which the fuel friction value does increase slightly.

Currently, the explanation for the differences in behavior of NFP-2 and NFP-3 is now known. However, it should be noted that NFP-2 is a fuel which has been severely hydrotreated and thus, only contains trace amounts of sulfur. In contrast, NFP-3 contains a large amount of sulfur (0.09% by weight) due to the fact that it had not been hydrotreated during processing. Thus, it is felt that the differences in behavior of these two fuels is probably related to the quantity and kinds of polar compounds present in each.

As seen thus far, a part of the data from the apparatus transfer and time/temperature tests could be used to update Figure 58 to more clearly define the trends toward decreasing fuel harshness with time and refrigeration. In the case of the fuel apparatus transfer test, only sample 21A should be included in the updated Figure 58 since this sample alone was drawn in a manner consistent with the other tests included in this figure. As seen in Table 52 and Figure 59 the effects of time and ambient temperature on previously refrigerated samples is generally to increase the harshness of the sample. Thus, only the last samples drawn for each test should be included in the updated figure. These samples, labeled 13A and 43A were each shipped out within a few hours of being removed from the refrigerator thereby minimizing the time at ambient temperature. Since this represents exactly the same situation as the previous tests used in Figure 58, these two data points are included in the updated plot. The result is Figure 60 which again shows the same trend of decreasing friction factors with time for refrigeration samples of fuel.

Of some interest is the effects of light, air and moisture on the lubricity of fuel samples. During the second quarter of this program, some repeat Lucas tests were performed on fuel samples that had been previously refrigerated and subsequently exposed to light and air. Although the data is not conclusive, the results suggest that the combined effect of light and air with time on fuel samples is in the direction decreasing friction factors. Since the ambient temperature on previously refrigerated fuel samples is in the direction of higher friction values, the combined effect of temperature,

light and air can be either toward a milder or harsher fuel depending upon the specific conditioning and the fuel involved.

In reviewing the literature, it appears that varying opinions exist concerning the role of water in fuel lubricity. To determine its effect, 1000 ppm of deionized water was added to various fuel samples. The fuel samples used were NFP-11, a JP-5 fuel received from Mobil Oil, Ashland 140, a JP-5 like solvent, and harsh isooctane. Apparently, the quantity of water was more than adequate to yield a saturated fuel since in each case it was reported by Cleveland that water droplets remained in the bottom of the pint fuel test bottles after vigorous shaking. The results of these tests as seen in Table 53 clearly shows that the friction factor in each case was decreased as a result of the addition of water. For NFP-11 and Ashland 140, the decrease in friction factors was about 10% while for the harsh isooctane, the reduction was about 5.5%. Although it is not known how water enters the lubricity picture, it has been suggested ⁽²³⁾ that water enhances the effectiveness of polar compounds, and, in particular, anticorrosion additives.

8.4.2 Additive Lubricity Test Approach

Based on the evaluation of test parameters as discussed in Section 8.4.1, it was found that certain variables such as temperature and possibly light, air and moisture could have a significant impact on fuel lubricity with time. It was also found that the Lucas tester yields repeatable, consistent data for fuel samples exposed to the same conditions and tested at roughly the same time. Thus it was concluded that meaningful results could be obtained on groups of fuel samples provided one sample is always included as a control or baseline test. Then the differences in fuel lubricities for each sample in comparison to the baseline result can, with confidence, be ascribed to the effect of the additive in the fuel and not to uncontrolled variables. It is on this basis that the Lucas tests were run from this point on.

8.4.3 Lucas Tests on Various Base Fuels

Since JP-5 as received from the refineries contains one or more additives, an alternative base fuel for additive testing was needed. Two candidates were selected for primary consideration. They are Ashland 140 and

Table 53.
Lucas Tests on Various Fuels With And Without Water Added

<u>Fuel Type</u>	<u>Additive in Fuel</u>	<u>Sample Number</u>	<u>Date Drawn</u>	<u>Date Tested</u>	<u>Conc. Water Added (PPH)</u>	<u>TRW/Lucas Friction Factor</u>
NFP-11	Yes	91A	6/13	6/17	0	.183
	Yes	92A	6/13	6/17	1000	.165
Ashland 140	Yes	64B	6/13	6/17	0	.193
	Yes	64C	6/13	6/27	1000	.171
Harsh Isooctane	No	121A	8/15	8/15	0	.512
	No	122A	8/15	8/15	1000	.484

Shell solvent 71. In addition, harsh isooctane was considered a possibility although this fuel is somewhat undesirable since corresponding BOCM runs are not possible. Previously, Ashland 140 was used in a Navy study ⁽²⁴⁾ while Shell solvent 71 has been utilized by the Air Force researchers at Wright-Patterson in their work ⁽²⁵⁾. To compare the fuels on an equal basis, Hitec E-515 was added to each at various concentrations.

Table 54 contains the test results on Ashland 140 solvent with and without Hitec E-515. As seen in the Table, two separate sets of test runs were performed with this solvent, both of which yielded comparable results. In the first case, samples 61A through 63A were individually prepared at Space Park and sent to Cleveland for testing. For the second set of runs, sample 64A was sent to Cleveland and tested after which sample 64B was prepared by adding Hitec E-515 to 64A. As evidenced by the data, it does not appear that any measurable facility bias in sample preparation exists since those data points which can be directly compared agree within 3% or less.

In examining the results of Table 54, it can be seen that Ashland 140 does not appear to be a suitable test fuel for additives. The basic problem is that this solvent is relatively mild, exhibiting a friction factor of about 0.2 which is between that of two JP-5 fuel samples, NFP-2 and NFP-3. Thus the effects of various additives would be expected to be at least partially masked. Indeed, this appears to be the case with both test runs where addition of HITEC did not produce any large changes in the friction factor.

Of some interest is the fact that the pure Ashland 140 solvent did not change in lubricity over a three month period. This is evidenced by the results of Samples 61A and 64A which yielded friction factors of 0.197 and 0.202, respectively. The primary difference between the handling of this fuel and that of NFP-2 and NFP-3 is that the Ashland 140 solvent was not stored in refrigeration. Thus this data tends to support the contention that NFP-2 and NFP-3 were changing in regards to lubricity due to refrigeration or a refrigeration-induced effect.

Table 55 contains the test results with Hitec E-515 in Shell Solvent 71. As seen by the data, samples 81A and 82A yielded considerably different results even though each sample was pure Shell solvent. Originally, when these samples were sent to Cleveland, the purpose was not for testing for this program. As a result, the normal fuel handling procedures were not followed

Table 54.
Lucas Tests on HITEC E-515 in Ashland 140

Sample Number	Date Drawn	Date Tested	HITEC E-515 Conc (ppm)	TRM/Lucas Friction Factor
61A	3/11	3/19	0.0	.197
62A	3/11	3/19	24.5	.195
63A	3/11	3/19	52.3	.193
64A	6/13	6/17	0.0	.202
64B	6/17	6/17	52.3	.193

Table 55.
Lucas Tests on HITEC E-515 in Shell Solvent 71

Sample Number	Date Drawn	Date Tested	HITEC E-515 Conc. (ppm)	TRM/Lucas Friction Factor
81A	4/20	5/27	0.0	.216
82A	4/20	5/27	0.0	.260
82B	5/27	5/27	52.3	.181

and contamination was suspected as discussed in Ref (26). In addition, it was reported by Cleveland that both fuel samples were leaking upon receipt, which is normally cause for sample rejection based on the possibility of contamination from the glue under the plastic cap foil seal. Therefore, the difference in test results are not surprising and point back to the need for careful handling of fuel samples.

Since contamination was suspected, it was concluded that the Shell Solvent 71 was at least as harsh as the friction value obtained with sample 82A. Thus, Hitec E-515 was added to this sample, now labeled 82B, and the result was a friction value of 0.181. Based on this result, it was concluded that Shell Solvent 71 was a harsh enough fuel for meaningful lubricity additive testing.

8.4.4 Final Selection of Additive Test Fuel

Based on the positive results obtained with Hitec E-515 in Shell Solvent 71 as discussed in the previous section, a series of Lucas runs were performed to determine how the additive behaves at various concentrations in the Shell solvent. In addition, a similar set of tests were performed with Hitec E-515 in isooctane as discussed later.

Table 56 contains the results of the test runs with Hitec E-515 added to the Shell solvent at various concentrations. As seen in the Table, the friction value of the pure Shell solvent (sample 141A) was 0.44, indicating a very harsh fuel. In comparing this value with the result of samples 81A and 82A it can be seen that the previous samples did in fact undergo some contamination resulting in lower friction values.

Figure 61 graphically displays the results of Table 56. As seen in Figure 61 and Table 56, Hitec E-515 reduces the fuel harshness of Shell Solvent 71 even when present in very low levels. Although the addition of 0.02 ppm of Hitec did not have a significant impact on fuel lubricity, the presence of 0.20 ppm resulted in a friction factor drop from 0.44 to 0.345. As shown in Figure 61 the measured friction factors decrease steadily with an increase in the log of the additive concentration with about 2.0 ppm after which no significant lubricity drops occur. This point, called the friction factor break point, represents the minimum concentration at which the additive

Table 56.

Lucas Tests on HITEC E-515 in Shell Solvent 71

<u>Sample Number</u>	<u>Date Drawn</u>	<u>Date Tested</u>	<u>HITEC E-515 Conc. (PPM)</u>	<u>TRW/Lucas Friction Factor</u>
141A	9/14	9/14	0.0	.44
142A	9/14	9/14	0.02	.438
143A	9/14	9/14	0.20	.345
144A	9/14	9/14	2.0	.157
145A	9/14	9/14	10.0	.155
146A	9/14	9/14	20.0	.219

Table 57.

Lucas Tests on HITEC E-515 in Harsh Isooctane*

<u>Sample Number</u>	<u>Date Drawn</u>	<u>Date Tested</u>	<u>HITEC E-515 Conc. (PPM)</u>	<u>TRW/Lucas Friction Factor</u>
71A	4/22	4/22	0.0	.61
72A	4/22	4/22	0.02	.473
73A	4/22	4/22	0.20	.336
74A	4/22	4/22	2.0	.170
75A	4/22	4/22	6.0	.183
76A	4/22	4/22	24.5	.182
77A	4/22	4/22	52.3	.166

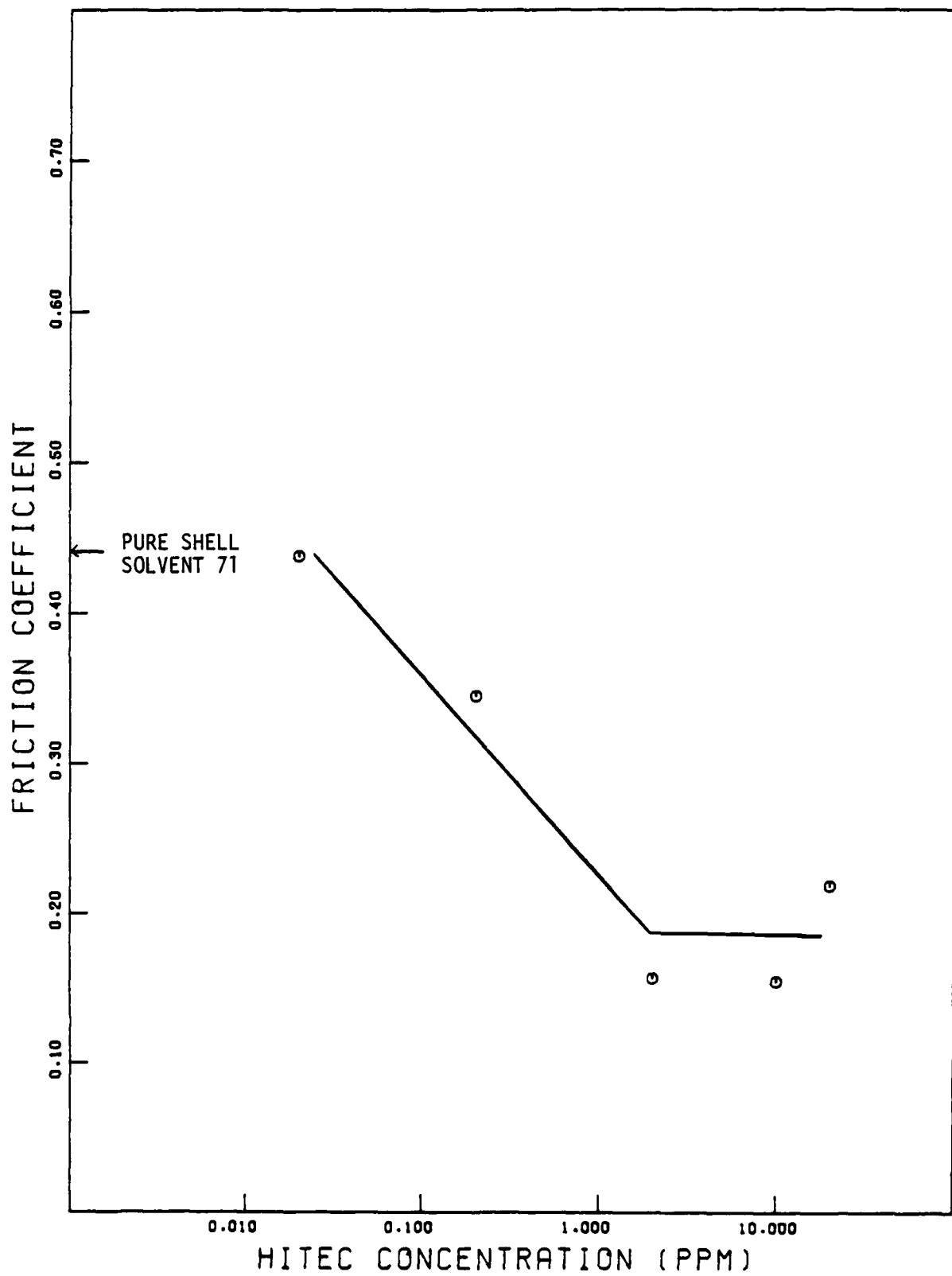


Figure 61. HITEC E-515 in Shell Solvent 71

obtains its maximum effectiveness in terms of lubricity. This result is significant since the qualified products list (QPL)⁽²⁷⁾ requires HITEC E-515 to be present in JP-5 at a minimum level of 24.5 ppm by volume and allows the concentration to be as high as 52.3 ppm. Thus, it is possible that the current levels of HITEC in JP-5 are excessive in terms of lubricity although this should be confirmed on a sample of JP-5 fuel.

As stated above, one of the primary reasons for performing tests on HITEC E-515 in isooctane is to determine how the results compare to those obtained with the additive in Shell Solvent 71. Table 57 contains the results obtained with Hitec in isooctane while Figure 62 graphically displays these results. For ease of comparison, Figure 63 is included which contains the Hitec/isooctane and the Hitec/Shell Solvent results on a single plot. As seen in Figure 63, the additive test results with Hitec in either fuel are roughly the same. In each case, the friction factor drops steadily with an increase in the log of additive concentration until about 2.0 ppm after which significant drops are not seen. The main deviation between the two sets of test runs is at 0.02 ppm of Hitec where the isooctane data showed a significant drop in friction factor while the Shell Solvent 71 data did not show a measurable change. However, this may be explained by the fact that the isooctane was initially much harsher than the Shell Solvent and thus, the effects of adding 0.02 ppm of Hitec were probably masked. Indeed pure Shell Solvent 71 is slightly milder than isooctane with 0.02 ppm of Hitec.

In examining the data of Figure 61 and 63 more closely, it can be seen that the Hitec/Shell Sol data contains a higher degree of scatter than the Hitec/Isooctane data. During the testing of the Shell Solvent, large vibrations were experienced due to fuel stick/slip problems on the disk. In addition, problems were encountered with oxidation of the fuel under the pin resulting in occasional low readings. In discussions with Rick Kamin of NAPTC, that facility also encountered vibrations and chatter when running Shell Solvent samples from TRW. Thus, it must be recognized that the data obtained with the Shell Solvent were not as good as the data obtained with isooctane. Since better data were obtained with isooctane as the base fuel and since neither fuel can consistently be used to obtain good BOCM data from NAPTC, it was decided to use isooctane as the standard test fuel for additive testing.

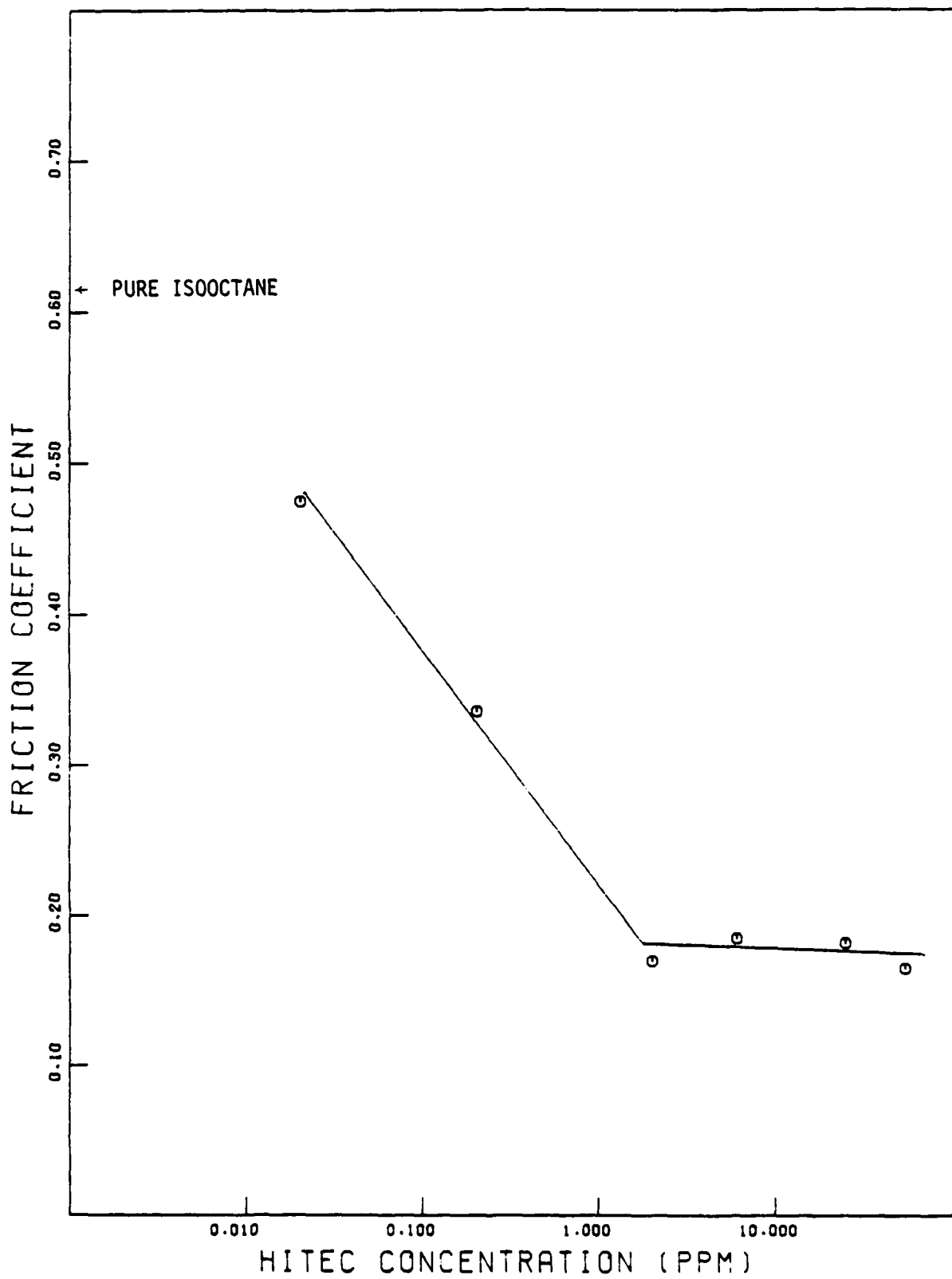


Figure 62. HITEC E-515 in Isooctane

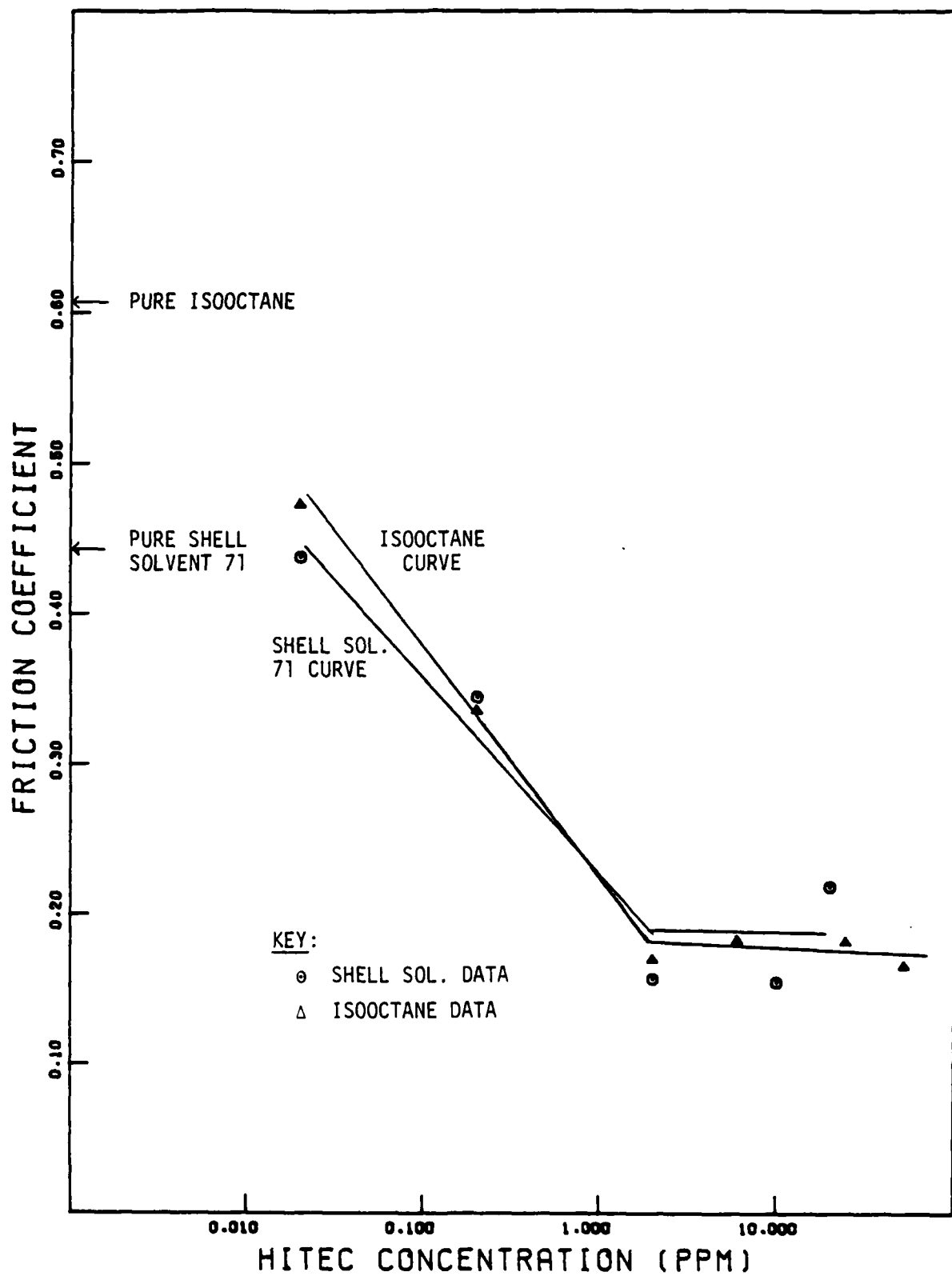


Figure 63. HITEC E-515 in Various Fuels

8.4.5 BOCM Tests with HITEC E-515 in Shell Solvent 71

A series of tests were performed on the BOCM with HITEC E-515 in Shell Solvent 71 in a manner similar to the Lucas tests discussed previously. As seen in Table 58, the BOCM yielded an extremely high wear scar value for the pure Shell Solvent (sample 131A) in the initial test run. Subsequent repeat runs on the same sample had to be aborted because the BOCM cylinder was experiencing high wear due to the harshness of the fuel. In addition, it was reported by Rick Kamin of NAPTC that the device was experiencing large vibrations and ball/cylinder chatter. These problems continued with both samples 132A and 133A which contained 0.2 and 2.0 ppm of HITEC E-515, respectively. In contrast, the Lucas machine saw a drastic reduction in friction value at additive concentrations of 0.2 and 2.0 ppm (Table 56) with the latter value being the friction factor break point. Thus, the Lucas machine indicates that only 2.0 ppm of HITEC E-515 is required to impart good lubricity characteristics to Shell Solvent 71 while the BOCM not detect any major changes in the fuel at that concentration.

In contrast to the problems experienced at low additive concentrations, the BOCM yielded relatively low wear scar values with 24.5 and 52.3 ppm of HITEC in Shell Solvent 71. For instance, sample 135A containing 52.3 ppm of HITEC yielded wear scar diameters of 0.345 mm and 0.339 mm for an average value of 0.342 mm. This result is consistent with that of a relatively mild fuel of the approximate harshness of NFP-3, a JP-5 containing DCI-4A. It may also be noted that sample 135A which contained the maximum allowable concentration of HITEC yielded a smaller wear scar than sample 134A with the minimum allowable concentration. This result agrees with the tests performed by the Air Force Aero Propulsion Laboratory⁽²⁵⁾ using Shell Solvent 71 and, if correct, points to a definite advantage in maintaining the maximum allowable concentration of HITEC in JP-5 at all times. Since a certain percentage of the additive is lost during storage in metal tanks, it may be necessary to increase the additive concentration above the allowable limit to insure maximum fuel lubricity based on the BOCM results. Again, based on the Lucas results this is not a problem since the fuels tested reach their maximum lubricity with only 2.0 ppm of HITEC.

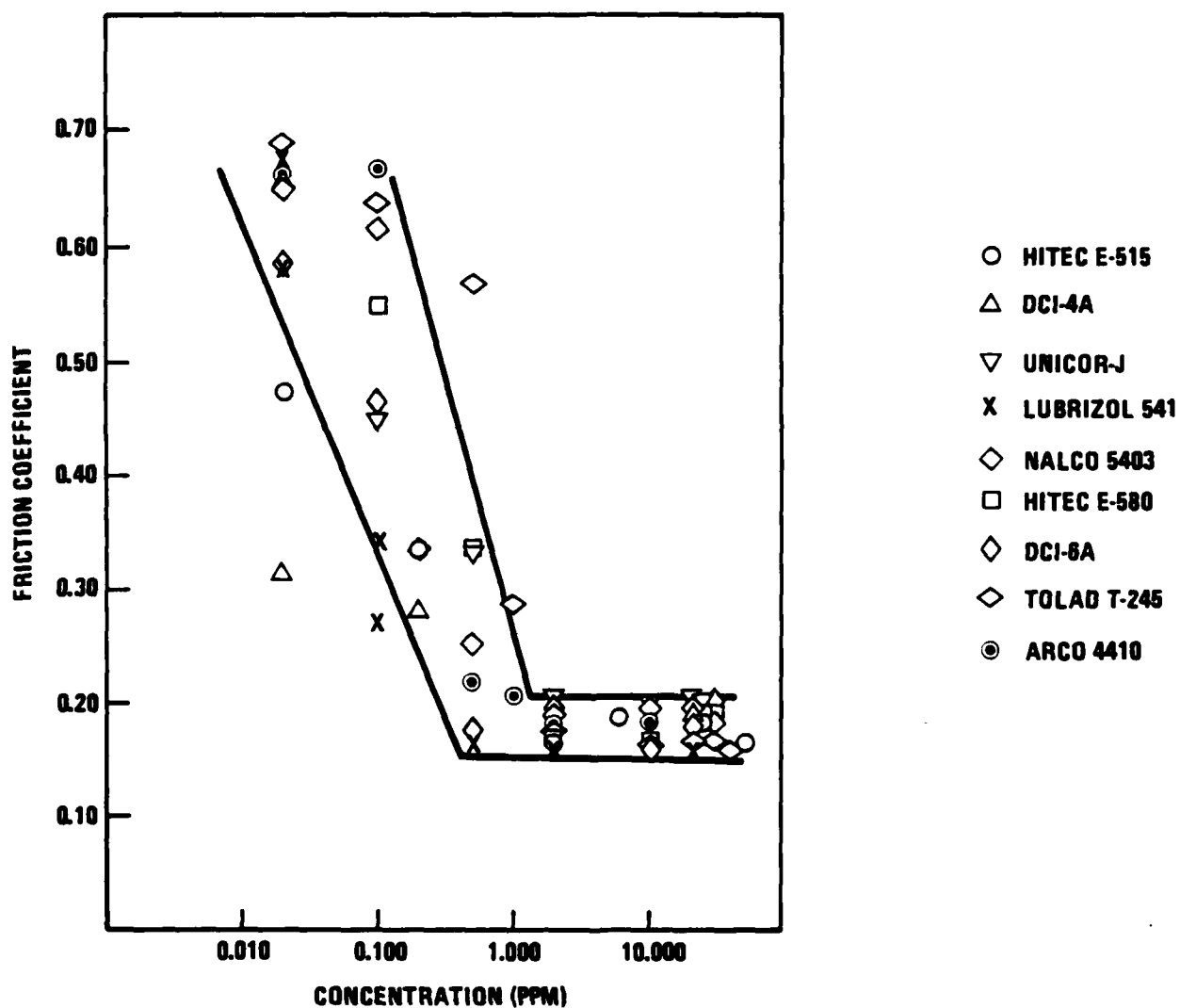
8.4.6 Lucas Test Results of Additives

During this program, a series of Lucas runs were performed on 10 different anticorrosion agents each individually tested in harsh isooctane at various concentrations. The result was that each of the 10 additives exhibited the same type of friction factor/concentration curve as seen with HITEC E-515 in isooctane although the effectiveness of the additives varied. To illustrate this in a concise manner, the results of all the additive/isooctane tests were grouped together in one plot labeled as Figure 64. A general discussion of additive behavior is now given after which a more detailed consideration of specific results will be presented.

Figure 65 shows an idealized plot of friction factor behavior versus additive concentration for the anticorrosion agents tested during this program. As seen in this figure, the measured friction factors steadily decrease with an increase in the log of the additive concentration until the friction factor break point is reached. At this point, the friction factors level off and remain relatively constant up to the concentrations tested. Within experimental error, each of the additives tested have followed this general trend. The distinguishing features of each additive appear to be the initial point of friction factor reduction and the break point. Of these two, the break point is the key parameter since it gives the minimum concentration at which the additive is most effective and it provides the friction coefficient pertaining to additive concentrations at or above the break point concentration.

Table 59 contains the additive key parameters experimentally determined in this program. Prior to considering the results of Table 59, it is necessary to discuss specifically how each data point is obtained. The initial friction reduction point is defined as the concentration at which the friction factor begins to drop from the original pure test fuel value. Hence, this number was determined for each additive by extrapolating each plot back to the harsh isooctane friction level and then reading the corresponding additive concentration on the X-Axis. In the case of the break point, the concentration value was visually determined from the plots while the

Figure 64. Summary of Friction Factor Data on All Qualified Additives in Isooctane



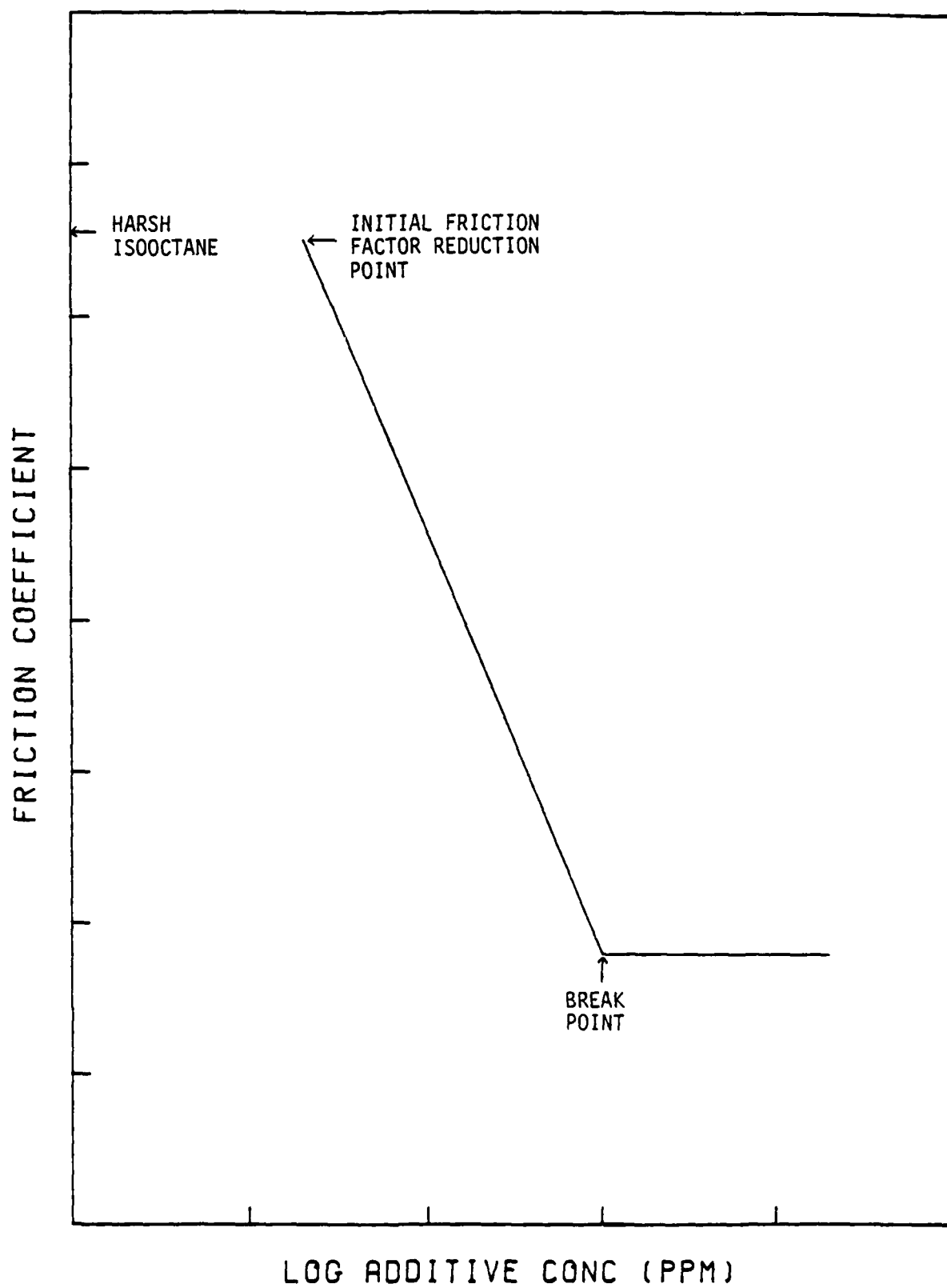


Figure 65. Idealized Plot of Anticorrosion Agent Behavior

TABLE 59. COMPARISON OF KEY PARAMETERS OF VARIOUS ADDITIVES

Additive Name	Pure Isooctane Test Fuel Friction Factor	Initial Friction Reduction Point		Break Point	
		Extrapolated Additive Conc (ppm)	Lowest Conc (ppm) Tested	Additive Conc (ppm)	Friction Factor
HITEC E-515	.61	.003	.02	2.0	.175
HITEC E-580	.65	.04	.02	2.0	.177
DCI-4A	.60	<.001	.02	2.0	.188
DCI-6A	.62	.02	.02	0.5	.185
NALCO 5403	.658	.02	.02	0.9	.189
UNICOR-J	.523	.06	.10	2.0	.203
LUBRIZOL 541	.70	.015	.02	0.2	.158
TOLAD T-245	.725	.015*	.02	4.2*	.163
ARCO 4410	.665	.02	.02	2.0	.186
MOBILAD F-800	.675	.01*	.02	0.8*	.182

*Approximate values. Data deviates from idealized curves.

corresponding friction factor was calculated by averaging all the friction data points at or above the break point concentration.

In examining the initial friction reduction point results of Table 59, it can be seen that each of the additives are capable of imparting a measure of lubricity to isooctane even when present at very low concentrations. Based on the extrapolated results DCI-4A is capable of imparting some lubricity to a harsh fuel at concentrations as low as 0.001 ppm (1 part per billion) while the first effects of UNICOR-J are seen at 0.06 ppm, still a very low concentration. As seen in the table, the other eight additives fall within this range of values. When considering these results, it should be noted that the values as reported in Table 59 are only valid for a harsh fuel such as isooctane. Essentially, this is because a milder fuel tends to mask the effects of the additive when present in low concentrations. Regardless, these data do serve to demonstrate the profound effect of the additives on fuel lubricity and provide clear proof of the sensitivity of the Lucas Tester.

In reviewing the break point results in Table 59, it is seen that only 0.2 ppm of Lubrizol 541 in isooctane is required for maximum lubricity effectiveness. DCI-6A, Mobilad F-800 and NALCO 5403 also had low break point concentrations as evidenced by values of 0.5, 0.8 and 0.9 ppm, respectively. The remainder of the additives had break point concentrations of about 2.0 ppm. This result is important since the QPL requires these additives to be present in jet fuels at concentrations of 8.9 to 24.5 ppm, depending on the additive (see Table 49). Thus, it appears that the current concentration levels of the additives in JP-5 are excessive in terms of lubricity and could be reduced if losses during fuel handling and storage are minimized.

Lubrizol 541 yielded the lowest break point friction factor encountered during this program. The value obtained with Lubrizol was 0.158 as compared to 0.175 for HITEC E-515. The remaining five additives yielded values from 0.163 for TOLAD T-245 to 0.203 for UNICOR-J. Based on this result and the break point concentration, it appears Lubrizol 541 is the most effective additive in terms of lubricity tested while UNICOR-J is the least effective. Next in effectiveness after Lubrizol 541 was TOLAD T-245 followed by HITEC E-515, the additive most commonly used in JP-5 fuel.

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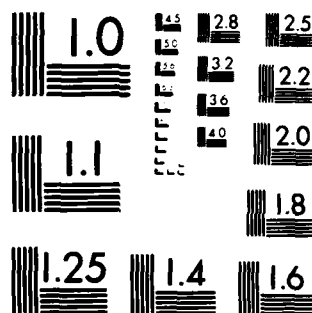
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8.4.7 Additive Comparisons with HITEC-E-515

Presently, the Navy is adding HITEC E-515 to JP-5 aboard their Pacific Fleet carriers for use in the F-14⁽²⁸⁾. In addition, it is understood that HITEC E-515 is the most widely used additive in JP-5 at this time. Thus, it is felt that a careful comparison of this additive with the others tested is in order. Accordingly, Figures 66 through 74 are provided to contrast the HITEC E-515/isooctane results with each of the other additives tested in isooctane thus far. Please note that the raw data used to generate the figures is included in Appendix E. The results are as follows:

- 1) Figure 66: HITEC E-515 versus DCI-4A
As seen in Figure 66, the DCI-4A additive appears to be superior to HITEC E-515 at concentrations below about 1.0 ppm. Above this concentration, HITEC appears to have a slight advantage. Each exhibits a break point concentration of about 2.0 ppm while HITEC has a lower break point friction value of 0.175 compared to 0.188 for DCI-4A.
- 2) Figure 67: HITEC E-515 versus UNICOR-J
In examining Figure 67, it is clear that HITEC E-515 is superior to UNICOR-J at all concentrations tested. Each exhibit a break point concentration of about 2.0 ppm but the break point friction factor for UNICOR-J is high at 0.203 compared to 0.175 for HITEC.
- 3) Figure 68: HITEC E-515 versus Lubrizol 541
As seen in this figure, Lubrizol 541 appears to be superior to HITEC E-515 at concentrations above about 0.09 ppm. As discussed previously, the Lubrizol additive has a significantly lower break point concentration and friction value than HITEC.
- 4) Figure 69: HITEC E-515 versus NALCO 5403
In reviewing Figure 69, it is apparent that HITEC E-515 generally outperformed the NALCO 5403 additive. The only advantage NALCO exhibited over HITEC was a lower break point concentration (compare 0.9 to 2.0 ppm) but it yielded a higher friction value (compare 0.189 to 0.175).
- 5) Figure 70: HITEC E-515 versus HITEC E-580
As seen in Figure 70, HITEC E-515 outperformed the HITEC E-580 additive up to the break point concentration of 2.0 ppm after which the additives behave virtually the same. The break point friction values of 0.177 for HITEC E-580 and 0.175 for HITEC E-515 are equivalent within experimental error.

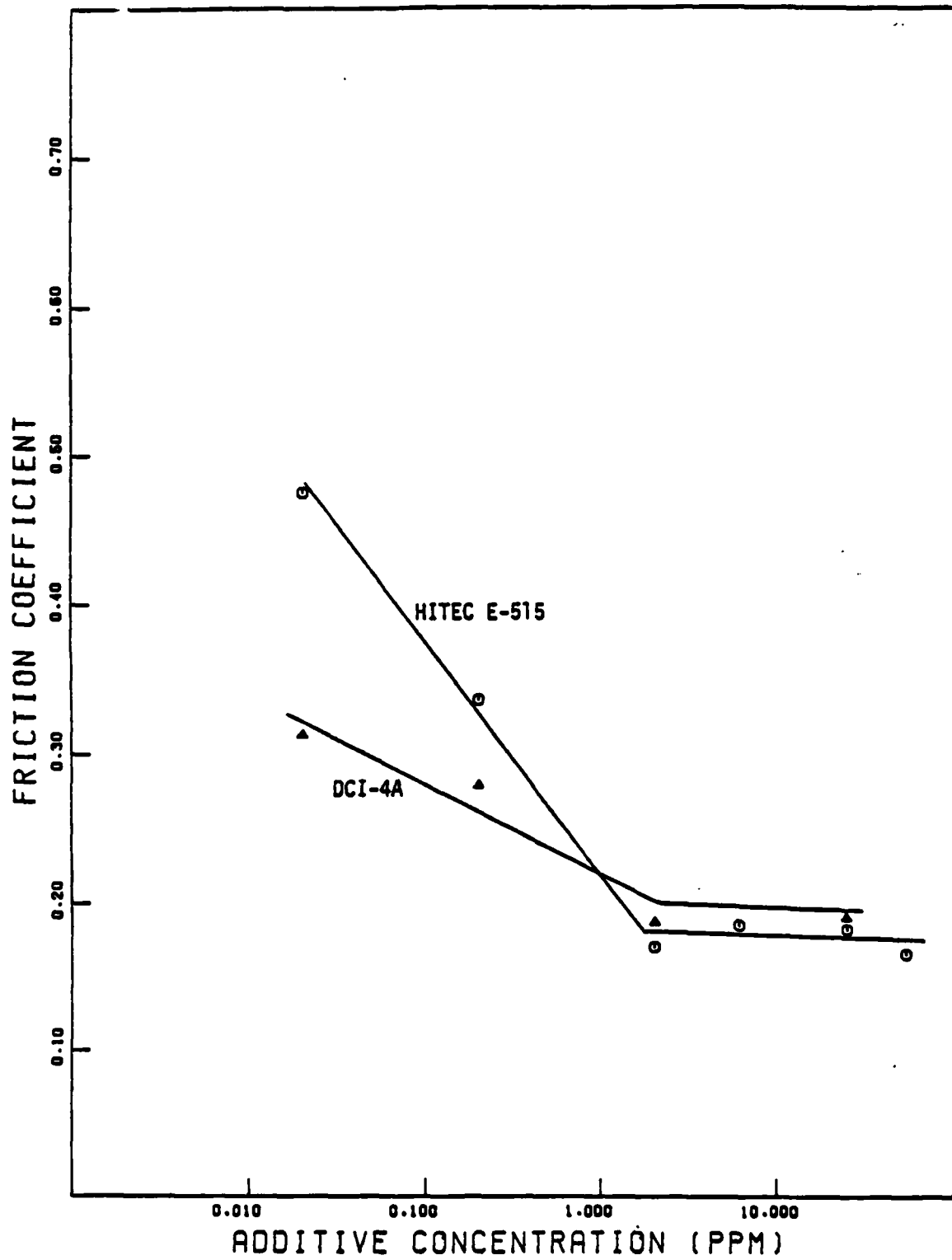


Figure 66. Comparison of HITEC E-515 and DCI-4A in Isooctane

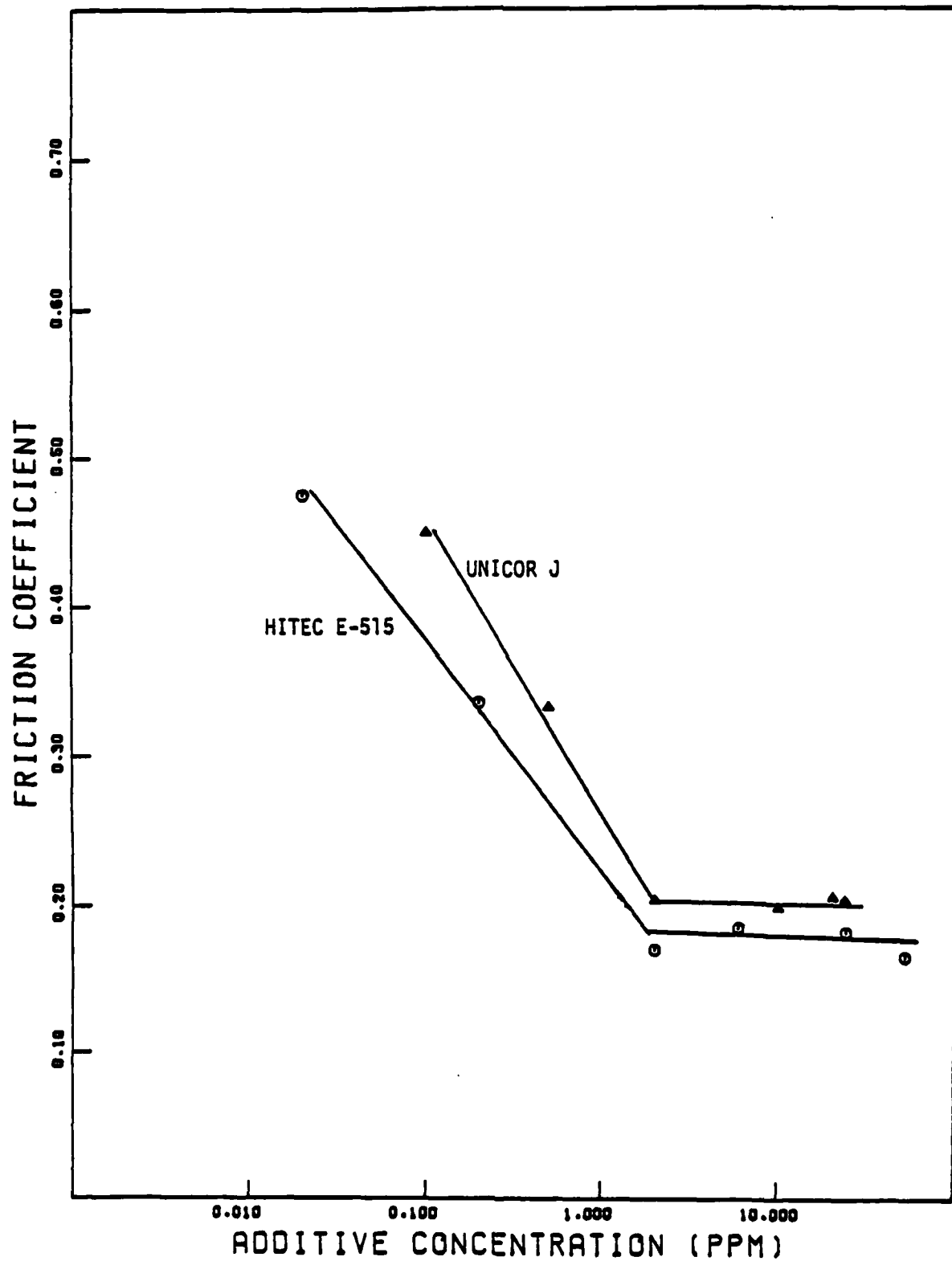


Figure 67. Comparison of HITEC E-515 and UNICOR-J in Isooctane

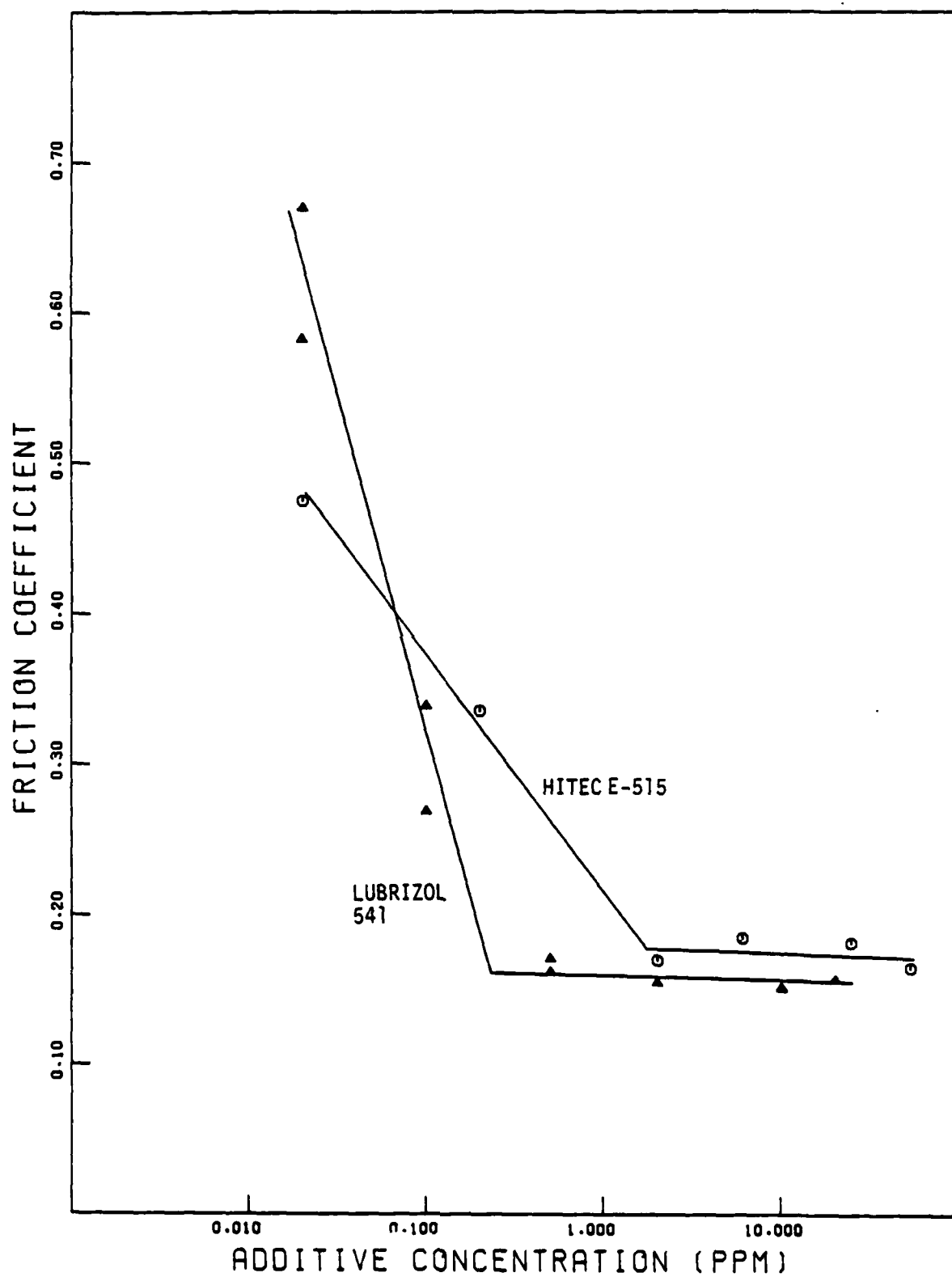


Figure 68. Comparison of HITEC E-515 and Lubrizol 541 in Isooctane

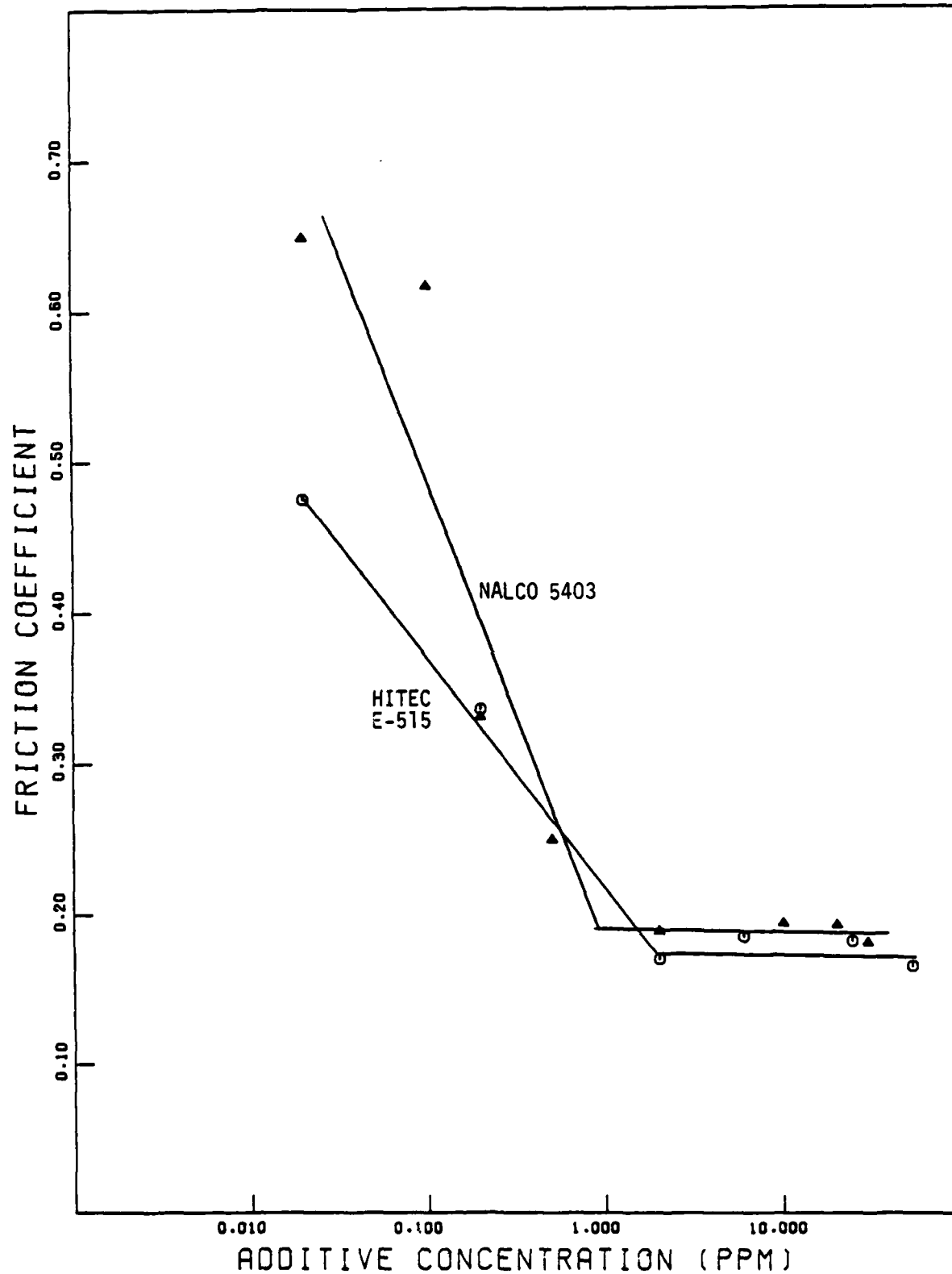


Figure 52. Comparison of HITEC E-515 and NALCO 5403 in Isooctane

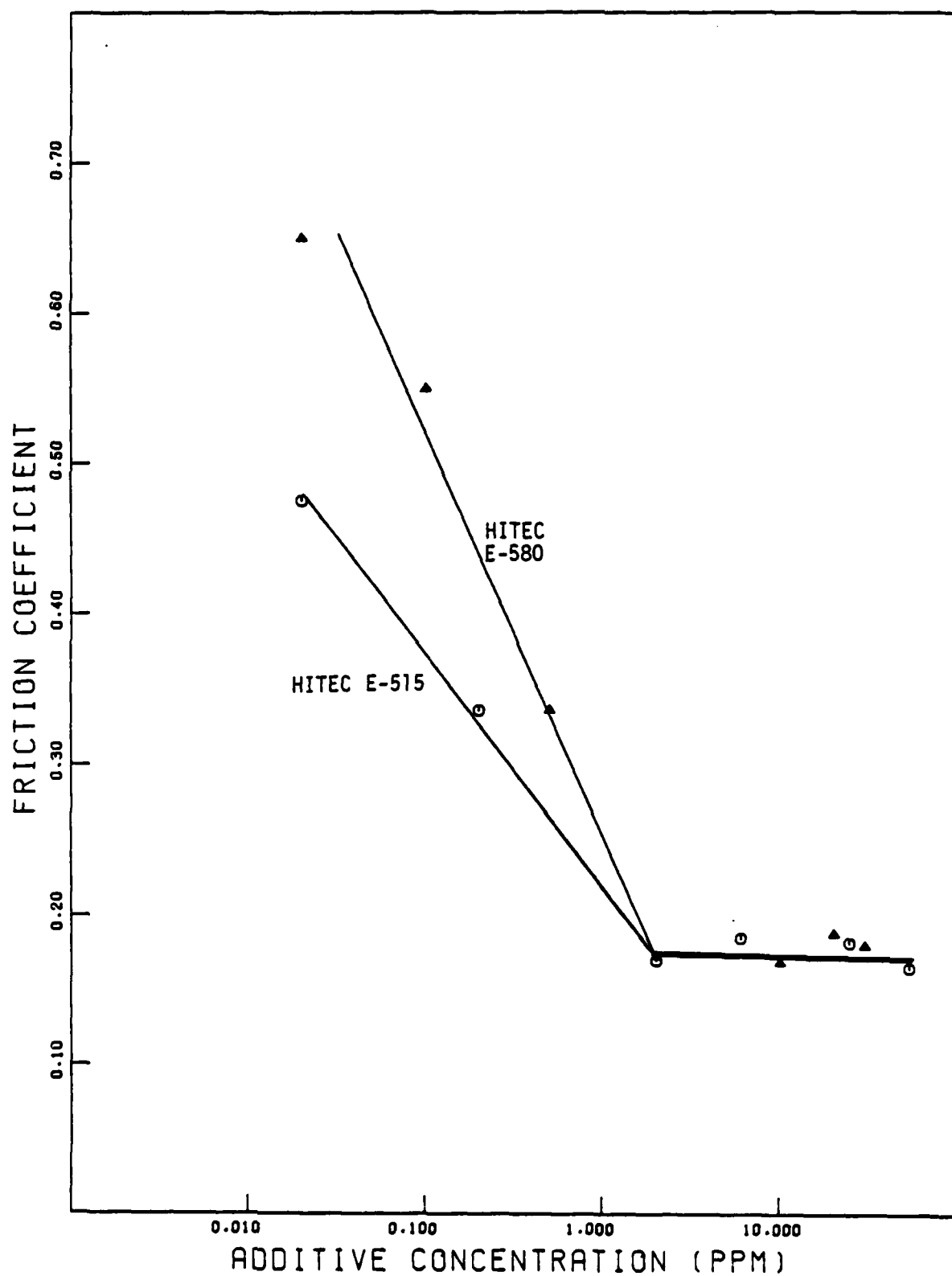


Figure 70. Comparison of HITEC E-515 and HITEC E-580 in Isooctane

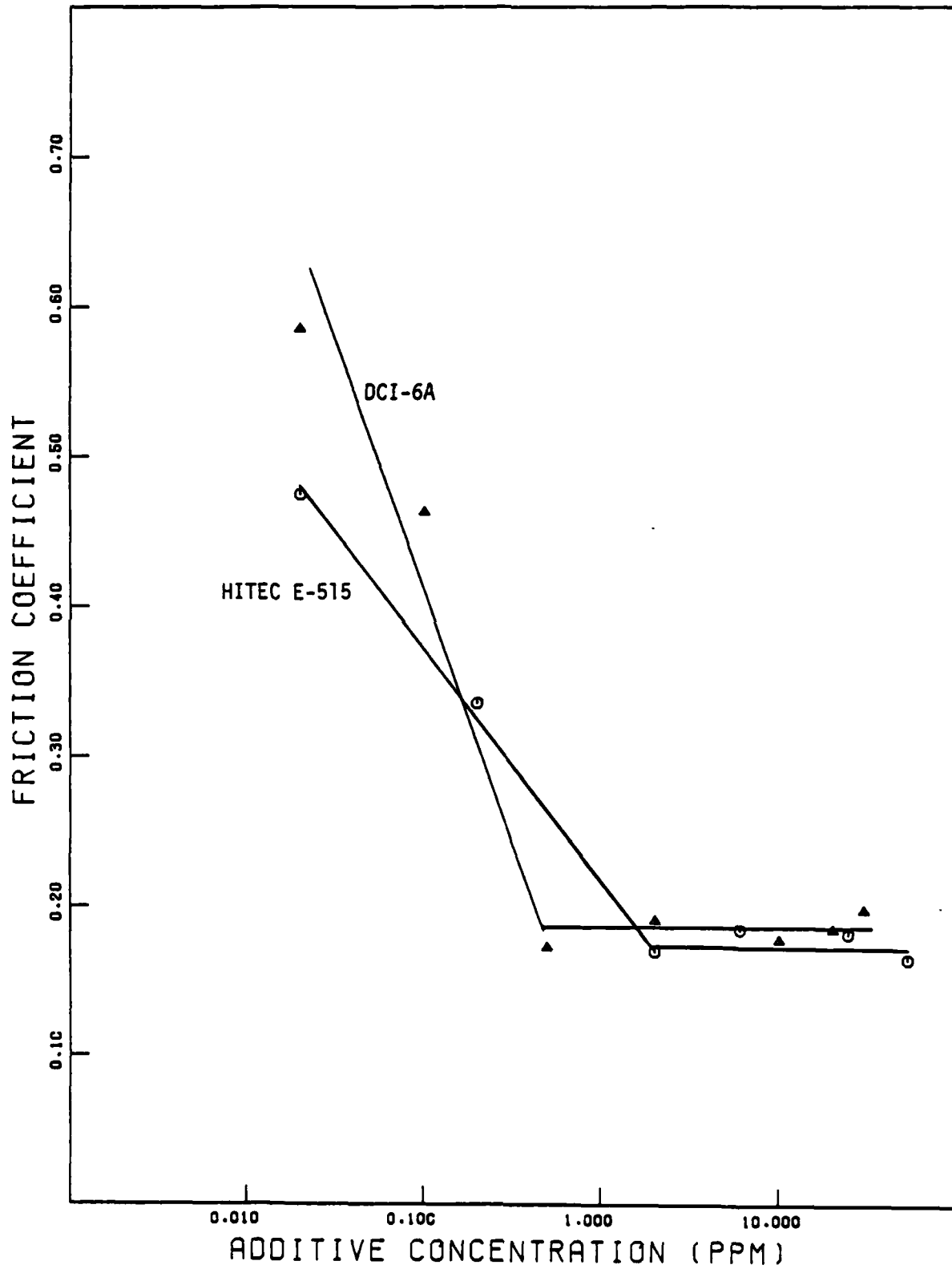


Figure 71. Comparison of HITEC E-515 and DCI-6A in Isooctane

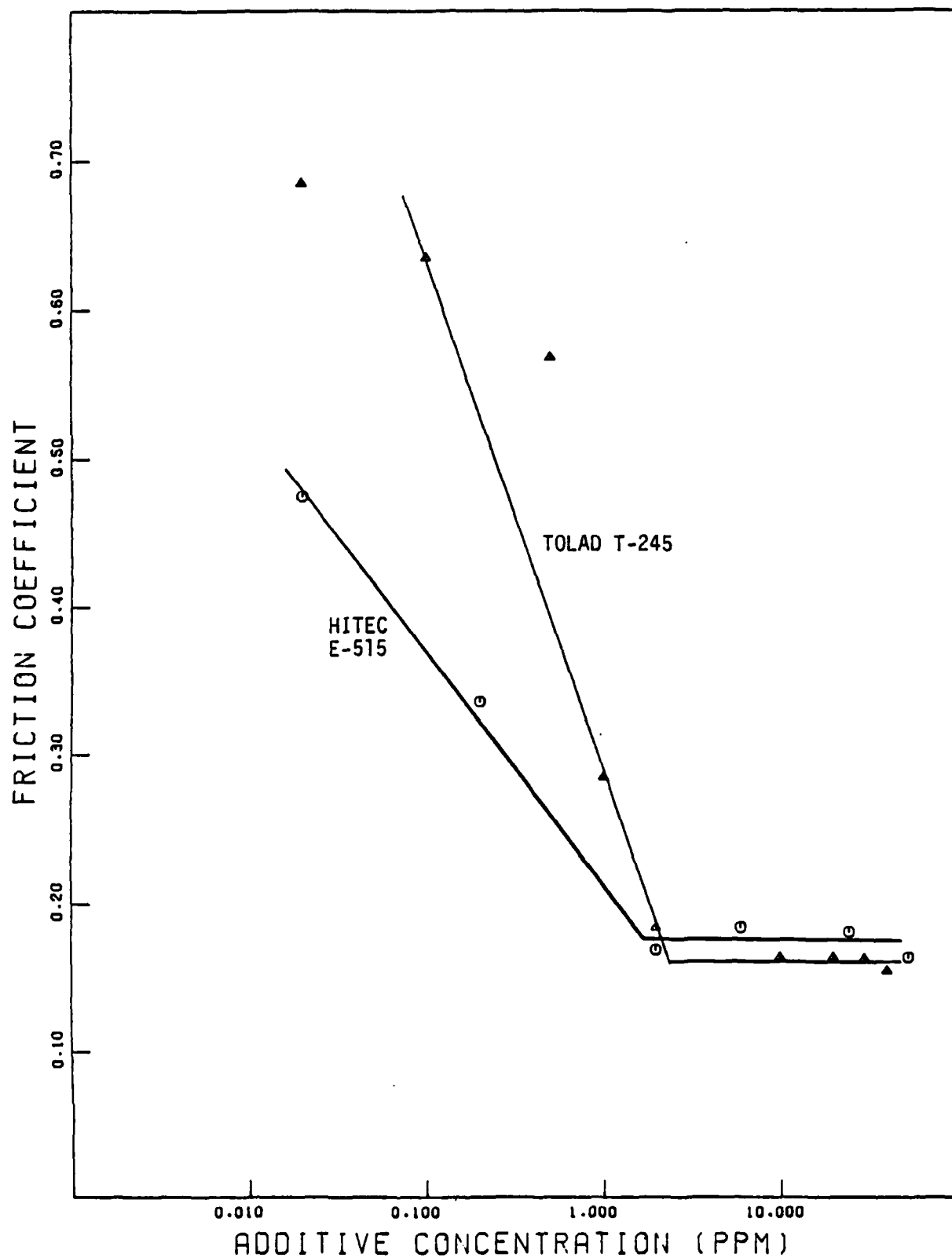


Figure 72. Comparison of HITEC E-515 with TOLAD T-245 in Isooctane

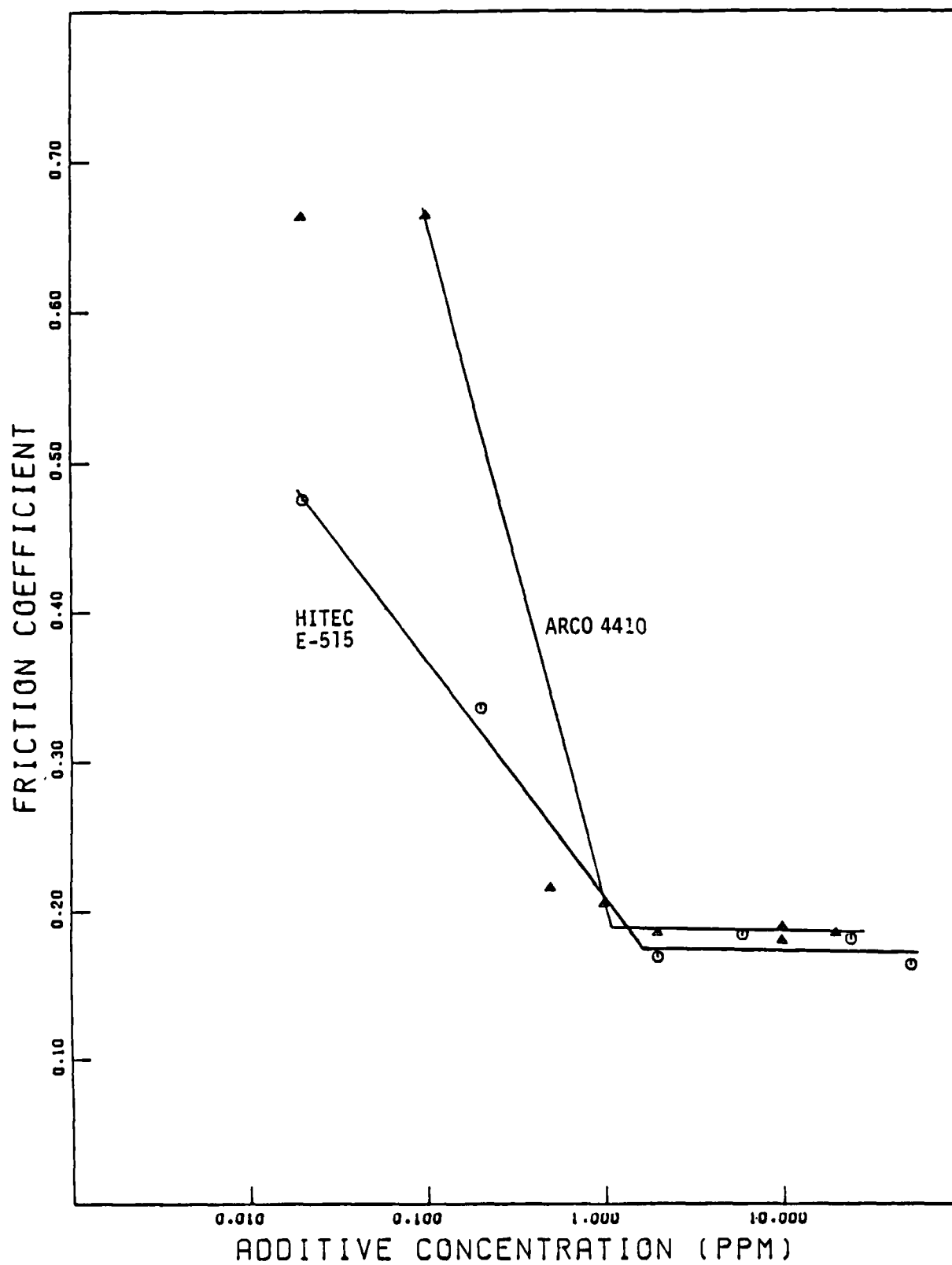


Figure 73. Comparison of HITEC E-515 and ARCO 4410 in Isooctane

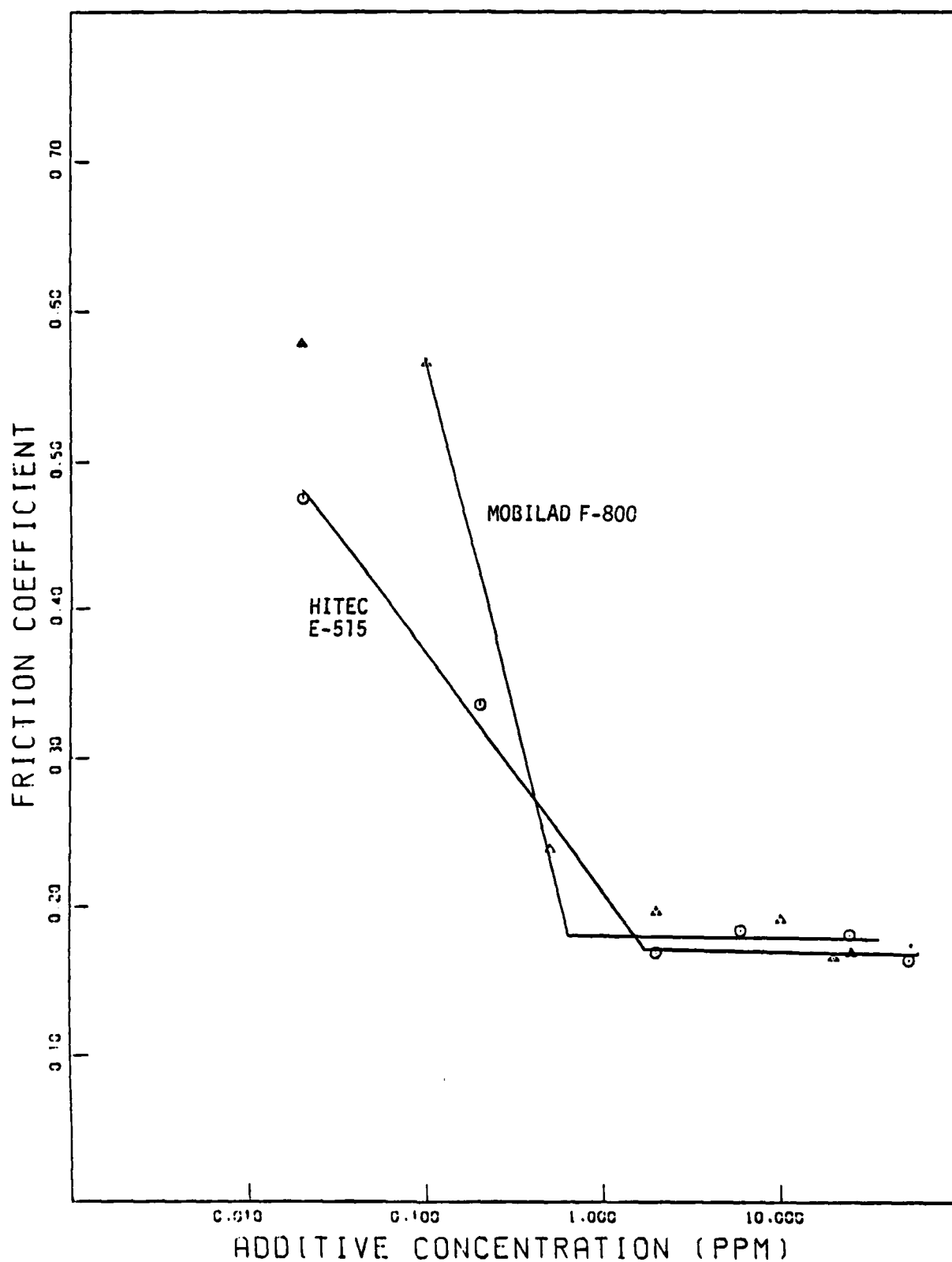


Figure 74. Comparison of HITEC E-515 and MOBILAD F-800 in Isooctane

- 6) Figure 71: HITEC E-515 versus DCI-6A
In reviewing Figure 71, it can be seen that HITEC E-515 generally outperformed the DCI-6A additive. However, the DCI-6A additive did exhibit a lower break point concentration than the HITEC (compare 0.5 to 2.0 ppm) but at a higher friction value (compare 0.185 to 0.175).
- 7) Figure 72: HITEC E-515 versus TOLAD T-245
As seen in the figure, TOLAD T-245 appears to be superior to HITEC E-515 at concentrations above about 3.0 ppm. The break point friction value for the TOLAD additive was 0.163 compared to 0.175 for HITEC.
- 8) Figure 73: HITEC E-515 versus ARCO 4410
In examining Figure 73, it can be seen that HITEC E-515 generally outperformed the ARCO additive. The only advantage exhibited by ARCO 4410 was a lower break point concentration but at a higher friction value (compare 0.186 to 0.175).
- 9) Figure 74: HITEC E-515 versus MOBILAD F-800
In reviewing Figure 74, it is seen that HITEC E-515 had a higher break point concentration than MOBILAD but resulted in a lower friction value.

8.4.8 Lucas Tests on FC-708

A series of Lucas tests were performed on the additive, FC-708, manufactured by the 3M company. Unlike the anticorrosion agents, FC-708 is strictly a lubricity additive for jet fuel. Based on the description received from the manufacturer, this additive is a fluorocarbon surfactant, and hence, is significantly different chemically from the anticorrosion agents tested. According to 3M, the effective concentration of this additive in jet fuel is about 200 ppm.

Table 60 contains the Lucas test results obtained when testing FC-708 at various concentrations in isooctane while Figure 75 displays these results. As seen in the figure, the behavior of FC-708 is considerably different from that of the anticorrosion agents. Not only does the lubricity curve appear different but the additive is seen to be relatively ineffective for lubricity even at concentrations of up to 1000 ppm. At 1000 ppm, the additive yielded a friction factor of 0.217, which would not improve the lubricity of a JP-5 fuel where values of about 0.20 are considered harsh.

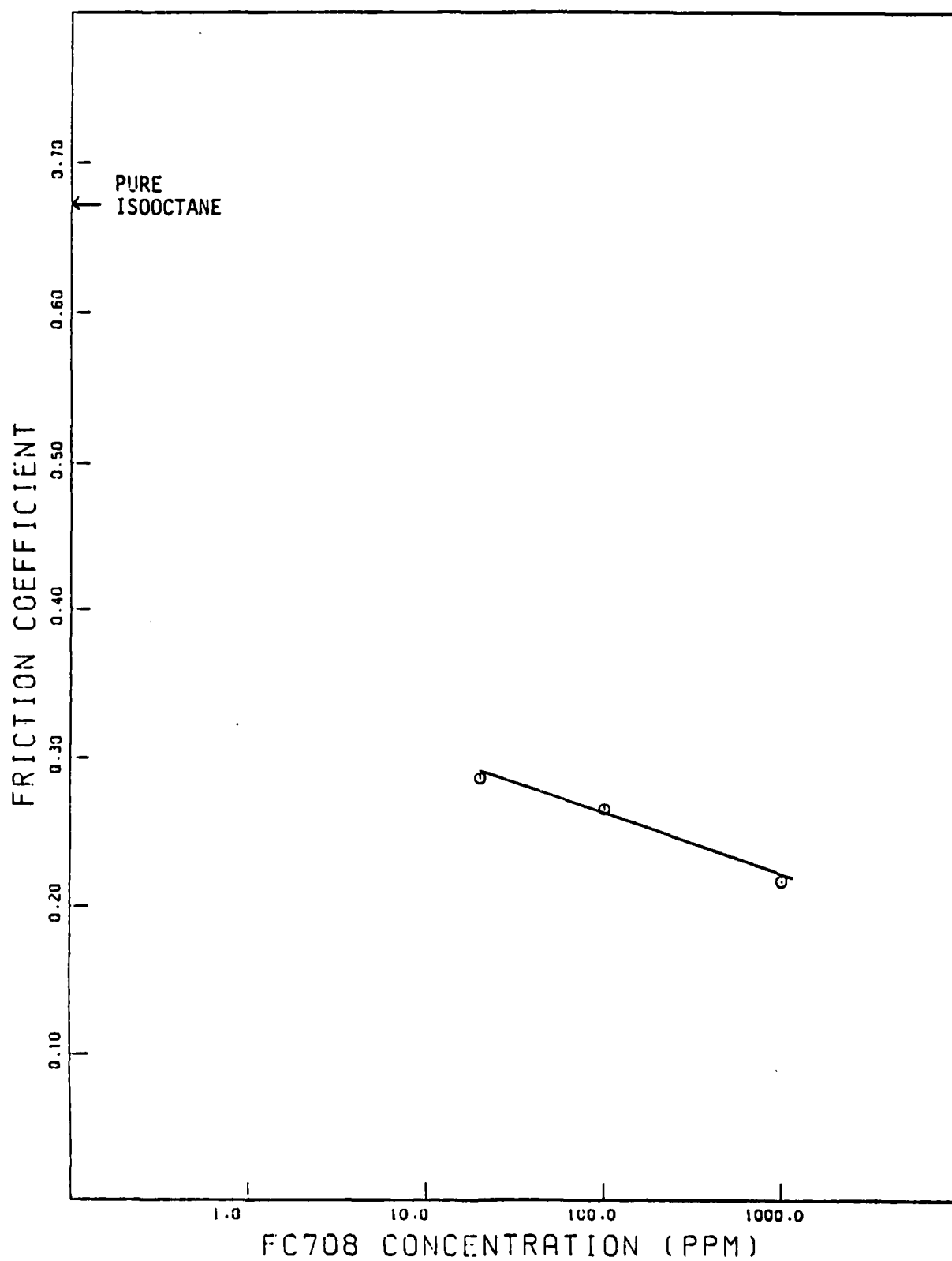


Figure 75. FC-708 in Harsh Isooctane

Table 60. Lucas Tests on FC-708 in Harsh Isooctane

Sample Number	Date Drawn	Date Tested	FC-708 Conc (ppm)	TRW/Lucas Friction Factor
251A	2/13/84	2/13/84	0.0	.675
252A	2/13/84	2/13/84	20.0	.286
253A	2/14/84	2/14/84	100.0	.265
254A	3/7/84	3/7/84	1000.0	.217

8.4.9 Lucas Tests on Sulfur Compounds in Isooctane

Since intensive hydrotreating of crudes creates harsh fuels and since such hydrotreating reduces the sulfur content of fuels, it has been assumed that sulfur containing species contribute to fuel lubricity. This assumption has been addressed using the identity of the prevalent sulfur containing species present in JP-5 gained in the Analytical Chemistry task in this program in combination with the reliable and meaningful lubricity testing procedure developed in this task.

The conclusion drawn, for which supporting data are presented below, is that those sulfur containing compounds normally present in JP-5 are not lubricity enhancers. It follows that the cause of the impact of hydrotreatment on lubricity is to be sought in some other changes in fuel chemistry, such as removal of polar hydroxy or carboxy functional organics or in the gross changes in ratios of saturated, cyclic saturated and aromatic compounds to each other.

Six sulfur containing compounds, listed in Table 61, were selected for this study. These are considered model fuel/sulfur compounds because they represent all the classes found in JP-5 and their boiling points are all within the JP-5 range.

The first Lucas test runs were performed on mixtures containing 20 ppm of each compound in harsh isooctane. If these compounds were effective lubricity enhancers one would expect that 20 ppm would result in the reduction of the friction factor by an amount approaching the reduction observed by the addition of 2 ppm of anticorrosion additives, such as HITEC E-515, which reduces the friction factor, typically, from 0.6 to 0.18 at 2 ppm. As seen

Table 61. Lucas Tests on Sulfur Compounds in Harsh Isooctane

<u>Sample Number</u>	<u>Sulfur Compound</u>	<u>Date Drawn</u>	<u>Date Tested</u>	<u>Sulfur Conc. (ppm)</u>	<u>TRW/Lucas Friction Factor</u>
231A	Butyldisulfide	2/2	2/2	0.0	.565
232A	Butyldisulfide	2/2	2/2	20.0	.58
233A	Octane Thiol	2/2	2/2	0.0	.605
234A	Octane Thiol	2/2	2/2	20.0	.421
235A	Dodecane Thiol	2/3	2/3	0.0	.606
236A	Dodecane Thiol	2/3	2/3	20.0	.557
237A	Benzothiophene	2/7	2/7	0.0	.687
238A	Benzothiophene	2/7	2/7	20.0	.516
239A	Dibenzothiophene	2/7	2/7	0.0	.577
240A	Dibenzothiophene	2/7	2/7	20.0	.530
241A	Octyl Sulfide	3/5	3/5	0.0	.648
242A	Octyl Sulfide	3/5	3/5	20.0	.578
271A	All 6 Above Added Together	4/11	4/11	0.0	.597
272A	All 6 Above Added Together	4/11	4/11	100 ppm each (600 ppm Total)	.319
273A	Benzothiophene, Dibenzothiophene Added Together	4/12	4/12	0.0	.715
274A	Benzothiophene, Dibenzothiophene Added Together	4/12	4/12	100 ppm each (200 ppm Total)	.633

in the last column of Table 61 the friction factor is only slightly affected, dropping by 16% on the average, ranging from 30% for octane thiol, to 8% for dibenzothiophene which is representative of the most prevalent class of sulfur compounds surviving hydrotreating. For butyldisulfide the change is slightly positive, but can be considered nil within experimental error.

One test of the lubricity of isooctane with 100 ppm of each compound added for a total sulfur concentration of 600 ppm (0.06%), a value frequently seen in low sulfur fuel, yielded a friction factor reduction from .597 to .319, a reduction by 57%. However the spiked fuel would still be considered very harsh.

The two aromatic thiophenes, compounds which survive hydrotreating, added to give a sulfur concentration of .02%, typical of hydrotreated fuels, only reduced the friction factor by 11%.

8.4.10 Lucas Test Results on di-Linoleic Acid in Isooctane

The main ingredient in most corrosion inhibitors which also function as lubricity enhancers is the dimer of linoleic acid. This information is generally known in the lubricity community and was confirmed by HPLC separation and IR analysis in this laboratory.

A second component often present is an unspecified ester of phosphoric acid known as the extreme pressure additive. We were not able to identify the phosphorous containing component here and did no further work on it. It may be assumed that each manufacturer adds other proprietary ingredients in small quantities.

The objective for this task was to compare the lubricity-enhancing behavior of the di-linoleic component with that of the total corrosion inhibitor. Unfortunately the time available for this task did not permit performance of a series of lubricity tests at extremely low additive concentration. Rather one test each at a concentration of 25 ppm was performed on each of two di-linoleic acid products: EMPOL 1022 and EMPOL 1010. These are both Emery Industries products.

The results, given in Table 62, show that friction factor reduction to about 0.2 is equivalent to the reduction achieved after the break point (defined in Figure 65) for all of the commercial anti-corrosion products (0.2 is slightly higher than average, See Figure 64). These results show that the lubricity enhancing characteristics of the anti-corrosion additives are mostly accounted for by their di-linoleic acid constituents. However, the extreme pressure additives are surely necessary ingredients for prevention of gear scoring under heavy loading.

8.4.11 Comparison of Lucas and BOCM Test Results

At the onset of this program, arrangements were made with Mr. Larry Graebel of the Naval Air Propulsion Center in Trenton, N. J., to perform BOCM tests on samples of the same fuel lots or mixture under test at TRW using the Lucas Tester. The careful analysis of fuel storage, packaging and aging, reviewed previously, was stimulated by the need to assure identity of test samples up to their introduction to either test device.

The untimely death of Mr. Graebel early in the program severely limited the extent of the collaboration. As a result, only 18 direct comparison tests were performed. Data from these tests are given in Table 63.

The BOCM device apparently could not perform smoothly with samples based on Shell Solvent 71. The viability of the BOCM to obtain data on extremely harsh fuels, always used for baseline information in Lucas testing, is seen here as a limitation on the application of BOCM testing to the resolution of fundamentals in lubricity science.

The comparison data are also presented in Figure 76 in order to show the extent to which a correlation may be drawn between Lucas test data on friction factors with BOCM data on wear scar diameters. The line in Figure 76 was drawn to show the least square fit of the data, ignoring Shell Solvent, BOCM results, which either aborted or fell off the chart.

Interpretation of these data is subjective. Three years of experience with the Lucas Tester, using very careful cleaning and calibration procedures as described in 8.3.3.1 gives us confidence that any friction factor reported is accurate to $\pm 5\%$. We believe that the friction factor is a measurement of a property of the fuel itself as a film performing boundary lubrication while

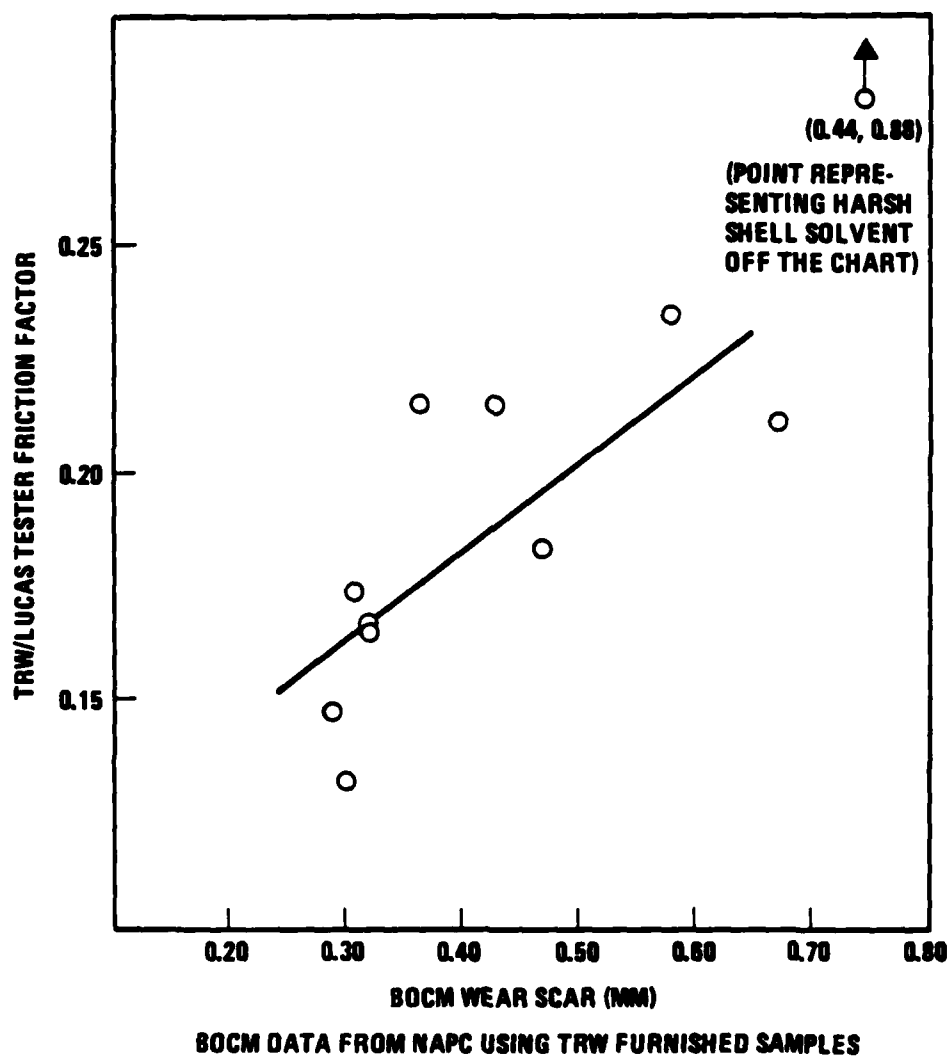
Table 62. Lucas Tests on Components in Harsh Isooctane

<u>Sample Number</u>	<u>Compound</u>	<u>Date Drawn</u>	<u>Date Tested</u>	<u>Compound Conc. (ppm)</u>	<u>TRW/Lucas Friction Factor</u>
301A		5/11	5/11	0.0	0.608
302A	EMPOL 1022	5/11	5/11	25.0	0.203
303A	EMPOL 1010	5/11	5/11	25.0	0.194

Table 63. Lucas Friction Factor vs. BOCM Scar

<u>Lucas Run</u>	<u>Friction Factor</u>	<u>BOCM Run</u>	<u>Wear Scar (MM)</u>	<u>Comments on Test/ Fuel Type</u>
1A	.234	1A	.58	First test on NFP-2
2A	.177	2A	.31	First test on NFP-3
3A	.212	3A	.67	Second test on NFP-2
4A	.167	4A	.32	Second test on NFP-3
11A	.162	14A	.32	Tests to determine the effects of time and refrigeration on NFP-3 fuel
12A	.147	15A	.29	
13A	.132	16A	.30	
91A	.183	93A	.468	Tests on NFP-11 with and without water added
92A	.165	94A	.406	
141A	.44	131A	.88	Pure Shell Solvent 71
143A	.345	132A	Aborted	Shell Sol 71 with .2 ppm of HITEC E-515 added
144A	.157	133A	Aborted	Shell Sol 71 with 2.0 ppm of HITEC E-515 added
146A	.219	134A	.425, .365	Shell Solvent 71 with 20 ppm of HITEC E-515 added
281A	.157	291A	.367	NFP-14 Fuel (JP-5)
282A	.152	292A	.383	NFP-14 Fuel with 1.0 ppm Lubrizol 541 added
283A	.149	293A	.489	NFP-14 Fuel with 5.0 ppm Lubrizol 541 added
284A	.154	2954A	.376	NFP-14 Fuel with 25.0 ppm Lubrizol 541 added
285A	.153	295A	.299	NFP-14 Fuel with 50.0 ppm Lubrizol 541 added

Figure 76. Comparison of Friction and BOCM Wear Scar Data
Obtained on the Same Fluids

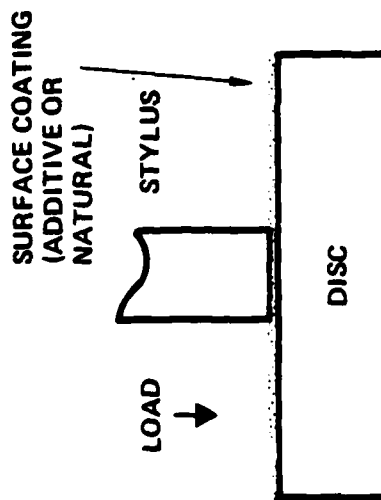


the BOCM wear scar, as a number, depends on relative humidity in the room, materials used for construction of the ball and the cylinder, ball/cylinder force, time over which a run is performed and a host of parameters other than the fuel. Fuel under test is certainly one of the key parameters in the BOCM test, but every other parameter must be held rigidly constant from test to test and from machine to machine if the wear scars are to be meaningful. The trend, seen in Figure 76, is for these fuels having the larger friction factor to yield a larger wear scar, but we also see three points with friction factors of 0.22 for which the wear scar diameters vary from 0.36 to 0.67 mm.

Other issues in comparing the two techniques are shown in brief on a recently prepared vu-graph shown here as Figure 77.

A correlation between friction factor and wear scar diameter such that the latter could be measured, and a friction factor obtained from a chart to be used for calculating the flash temperature is a realistic goal but one far from attainment at this time. TRW is of the opinion that imposition of wear scar diameter criteria to fuel or fuel pump qualification should await a demonstration that the BOCM method has been standardized to the extent of being sensitive to lubricity only.

Finally we present in Figure 78 a plot of those results on wear scar diameter vs additive concentration now available to TRW. The concentration scale has been made logarithmic for comparison with Lucas test data plotted in this report. We note the linear relation of wear scar to log concentration with one point obtained at Esso hinting at a similar plateau phenomenon as observed here, but displaced upwards from 2 ppm to 20 ppm.

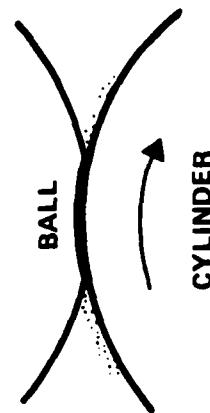


TRW/Lucas

- No wear of disc or stylus
- Fuel surface layer intact
- Friction factor independent of vertical load (5 loads for validation)

Force dragging stylus along disc

$$FF = \frac{\text{Force dragging stylus along disc}}{\text{Vertical force on stylus}}$$

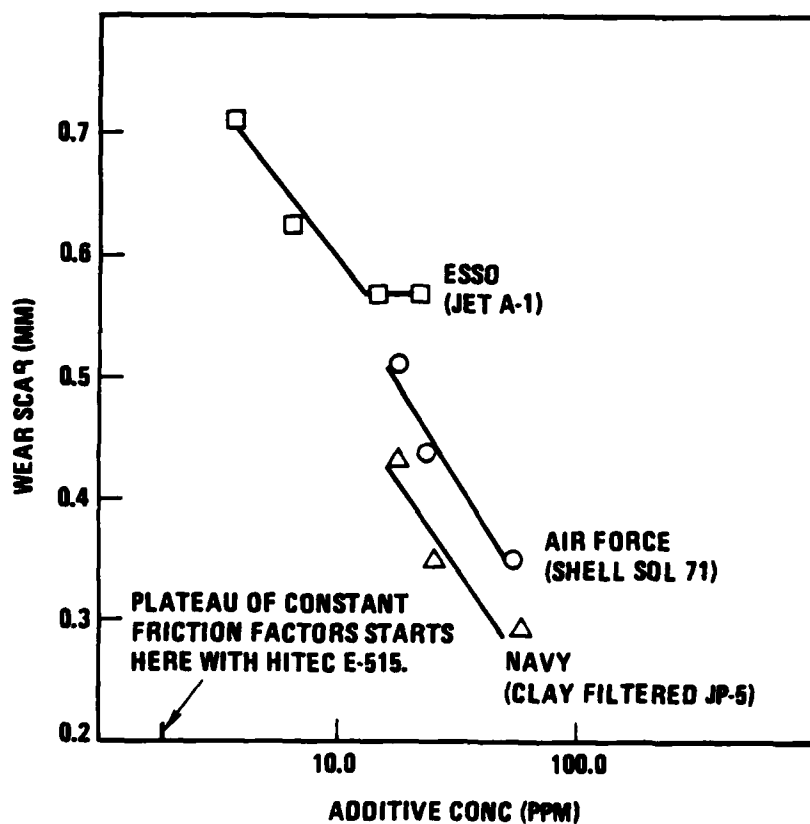


BOCM

- Scar formed by mild wear
- Fuel surface layer largely displaced
- Fresh metal surface, sensitive to relative humidity

Figure 77. Detailed Action of TRW/LUCAS Tester Compared with BOCM

Figure 78. Comparison of Wear Scar Diameters as Affected by HITEC E-515 Concentrations (Log Scale)



9.0 REFERENCES

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APPENDIX A.

Since fuel samples received for this project are likely to be used in more than one task, a number has been assigned to each sample for the program. The task reports will then refer to the sample number, which can be referred to this table for full description of the samples.

<u>Program Number</u>	<u>Refinery Source</u>	<u>Date Received</u>	<u>Comments</u>
NFP 1	Powerine	10 October 1982	One gallon, high sulfur JP-5 shipped from NRL, designated NRL 80-5.
NFP 2	Exxon, Banicia	15 October 1982	Five gallon JP-5 distilled from 90% North Slope 10% San Joachin Valley crude. Heavily hydro-treated - no A/O 35 added.
NFP 3	Powerine	10 November 1982	One gallon picked up at refinery, JP-5. Designated TL-88 by Powerine.
NFP 4	Mobil	5 September 1981	One pint JP-4, picked up at refinery.
NFP 5	National Bureau of Standards		NBS sulfur in distillate fuel (0.211%).
NFP 6	n.a.	10 December 1982	1 gallon, JP-5, shipped by NAPL.
NFP 7	Powerine		5 Gallons JP-5
NFP 8	Ashland	8 March 1983	5 Gallons, Ashland 140 Solvent. Similar boiling range to JP-5. No additives.
NFP 9	Shell	9 March 1983	5 Gallons, Shell solvent 71. Comparable to Ashland 140.
NFP 10	BEACON	10 May 1983	5 Gallons of JP-5 delivered in a 5 Gallon can.
NFP 11	MOBIL	10 May 1983	5 Gallons of JP-5 picked up at refinery in glass gallon jugs.

APPENDIX B
GC/MS ANALYSIS OF THE
PASH FRACTION OF NFP-1

Table B-2. GC/MS Analysis of NFP-1 PASH Fraction
(Figure A1)

Peak Number	Scan Number	GC Retention Time, min	Peak Area	Assignment ⁽¹⁾	Peak Number	Scan Number	GC Retention Time, min	Peak Area	Assignment ⁽¹⁾
1	1700	14:10	6560	BT(H ₂)	37	2385	19:52	14026	BT-C ₄
2	1794	14:57	133734	BT-C	38	2398	19:59	9251	BT-C ₄
3	1800	15:00	15251	BT-(H ₂)C ₁	39	2406	20:03	61725	BT-C ₄
4	1827	15:13	57736	Nph-C ₁	40	2423	20:11	21689	BT-C ₄
5	1841	15:20	7529	BT(H ₂)C ₂	41	2431	20:15	3671	BT-C ₄
6	1904	15:52	15928	BT(H ₂)C ₃	42	2438	20:19	12796	BT-C ₅
7	1925	16:02	67621	BT(H ₂)C ₂	43	2445	20:22	26790	BT-C ₄
8	1975	16:27	20169	BT(H ₂)C ₂	44	2456	20:28	19810	BT-C ₄
9	1989	16:34	45478	BT-C ₂	45	2463	20:31	6033	BT-C ₄
10	2003	16:41	83492	BT-C ₂	46	2467	20:33	1367	BT-C ₅
11	2029	16:54	104488	BT-C ₂	47	2475	20:37	15225	BT-C ₄
12	2044	17:02	115195	BT-C ₂	48	2492	20:46	12467	BT-C ₅
13	2075	17:17	42431	BT-C ₂	49	2502	20:51	3362	BT-C ₅
14	2083	17:21	255141	BT-C ₂	50	2522	21:01	9640	BT-C ₅
15	2122	17:41	27959	BT-C ₃	51	2534	21:07	4230	BT-C ₅
16	2128	17:44	15252	BT(H ₂)-C ₄	52	2539	21:09	1220	BT-C ₅
17	2138	17:49	24140	BT(H ₂)-C ₃	53	2545	21:12	4957	BT-C ₅
18	2148	17:54	15123	BT(H ₂)-C ₄	54	2551	21:15	10796	BT-C ₅
19	2164	18:02	4065	BT(H ₂)-C ₄	55	2564	21:22	5058	BT-C ₅
20	2184	18:12	18596	BT(H ₂)-C ₃	56	2570	21:25	2060	BT-C ₅
21	2194	18:17	101006	BT(H ₂)-C ₃	57	2576	21:28	6930	BT-C ₅
22	2207	18:23	50775	BT-C ₃	58	2596	21:38	6603	BT-C ₅
23	2224	18:32	22424	BT-C ₃	59	2606	21:43	10412	BT-C ₆
24	2233	18:36	26896	BT-C ₃	60	2649	22:04	4749	BT-C ₆
25	2239	18:39	49617	BT-C ₃	61	2683	22:21	1514	BT-C ₆
26	2257	18:48	44577	BT-C ₃	62	2695	22:27	42341	DBT
27	2262	18:51	94892	BT-C ₃	63	2709	22:34	1919	BT(H ₂)-C ₆
28	2278	18:59	5190	BT(H ₂)-C ₄	64	2739	22:34	1201	BT-C ₆
29	2294	19:07	134644	BT-C ₃	65	2751	22:55	788	BT-C ₇
30	2305	19:12	14495	Nph-C ₃	66	2789	23:14	3158	BT-C ₆
31	2311	19:15	11904	Nph-C ₃	67	2866	23:53	26332	DBT-C ₁
32	2337	19:28	23416	Nph-C ₃	68	2899	24:09	12599	DBT-C ₁
33	2348	19:34	7762	BT-C ₄	69	2939	24:29	8257	DBT-C ₁
34	2354	19:37	23095	BT-C ₄	70	3107	25:53	1810	DBT-C ₂
35	2367	19:43	36340	BT-C ₄	71	3177			DBT-C ₃
36	2377	19:48	16797	BT-C ₄					

(1) BT = Benzothiophene

(H₂) = dihydro

DBT = Dibenzothiophene

Nph = Naphthalene

C₁, C₂ ... = methyl, dimethyl (or isomers thereof) substituted

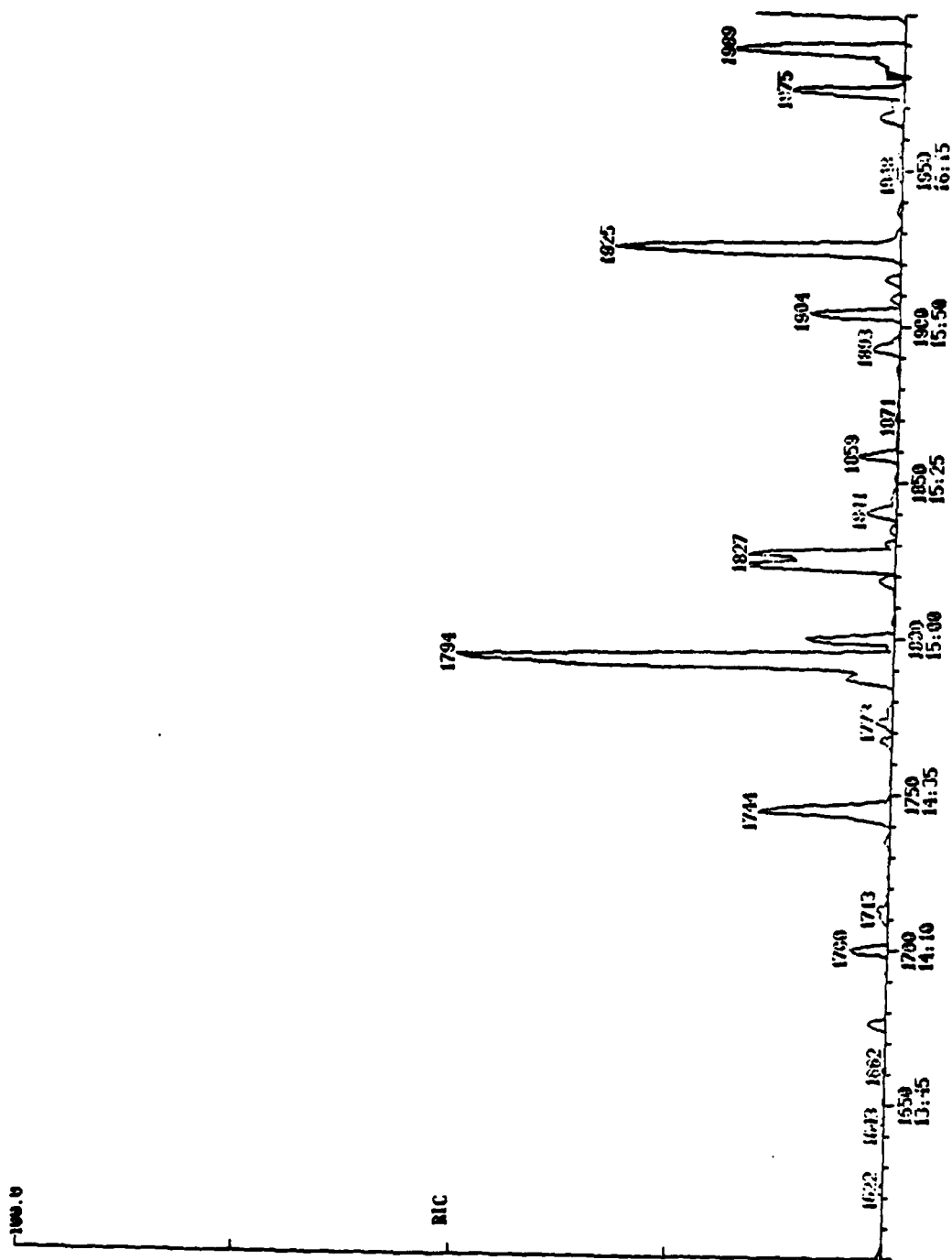


Figure B-1. Expanded Scale GC/MS Chromatogram of the PASH Fraction of NFP-1 (see Figure 1).
 a) Scans 1600 - 2000
 See Table B-1 for peak assignments.

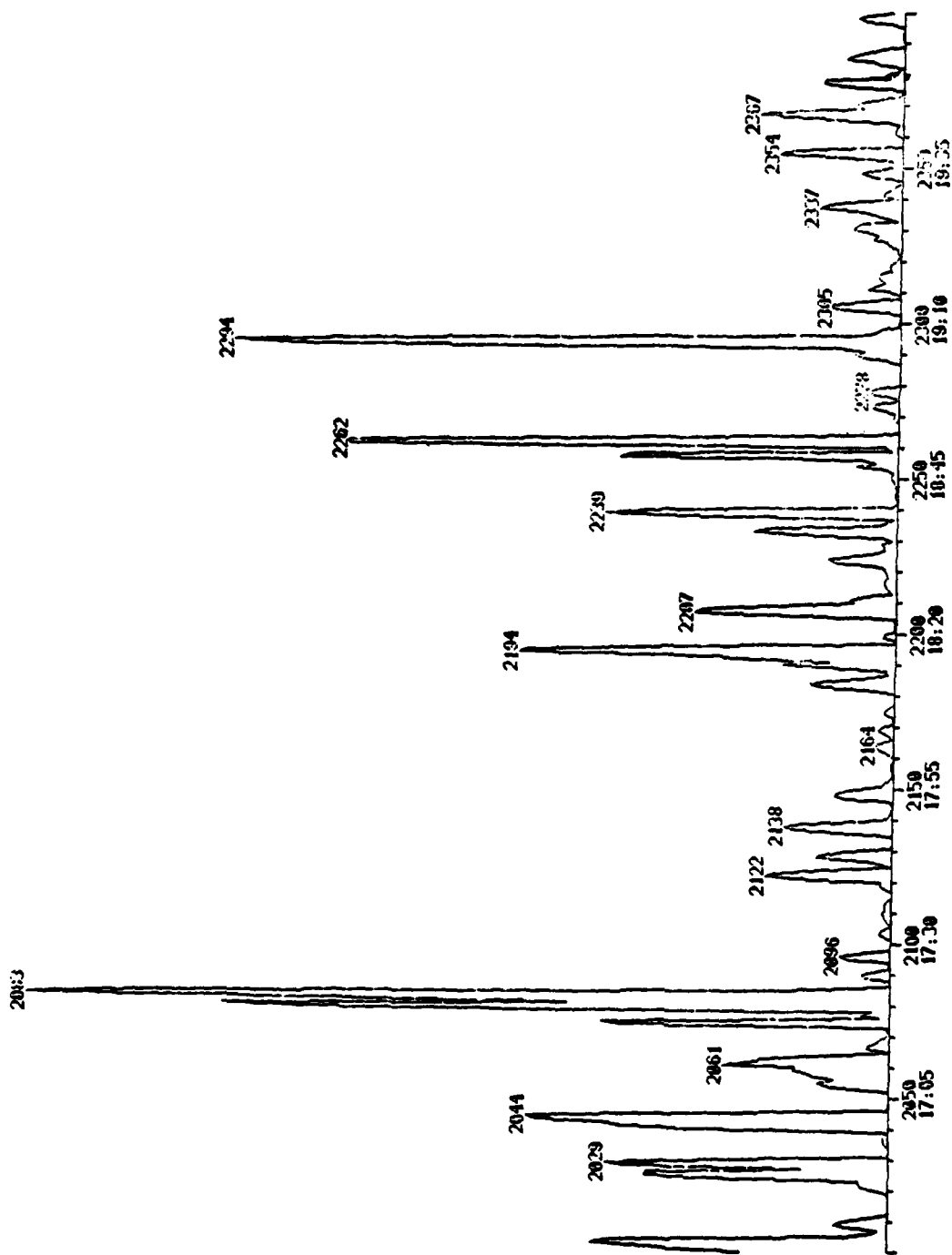


Figure B-1. b) Scans 2000-2400

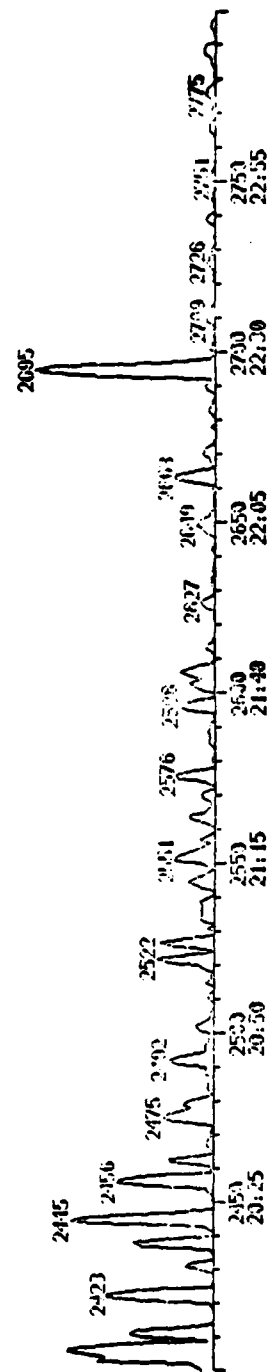


Figure B-1. c) Scans 2400-2800

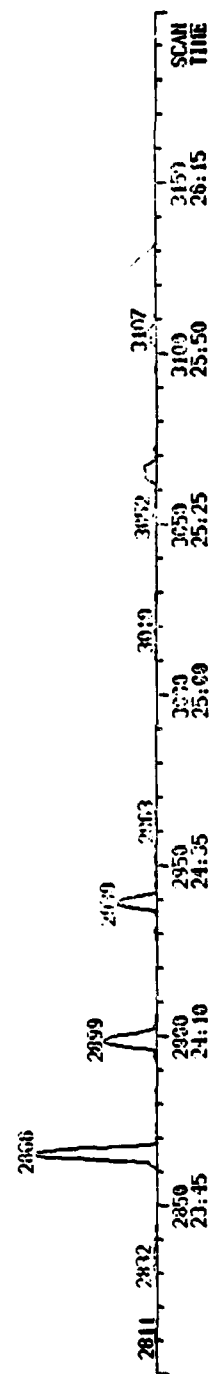


Figure B-1. d) Scans 2800-3200

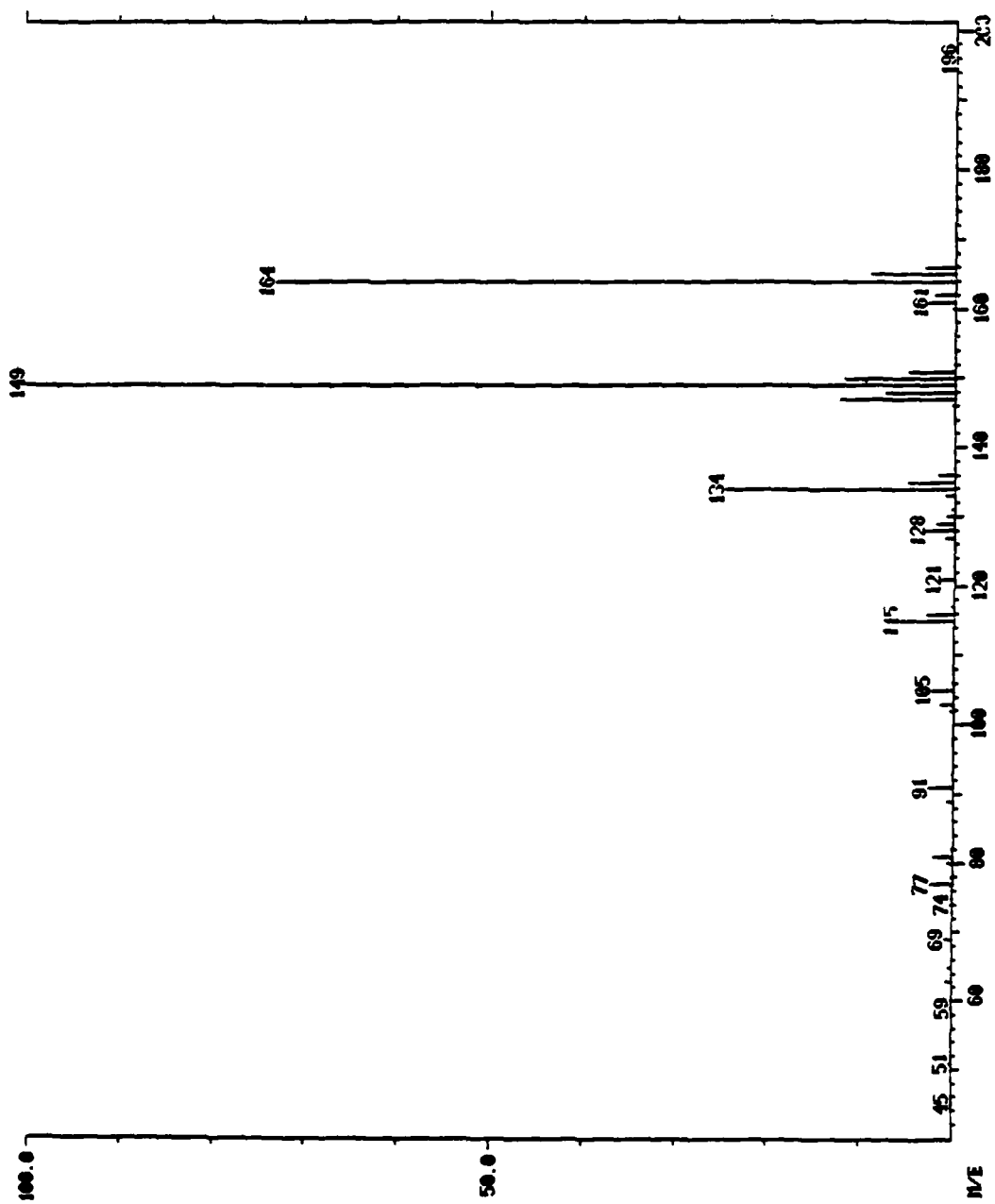


Figure B-2. Mass Spectrum of C₂-Dihydrobenzothiophene, Figure A-1, Scan No. 1925

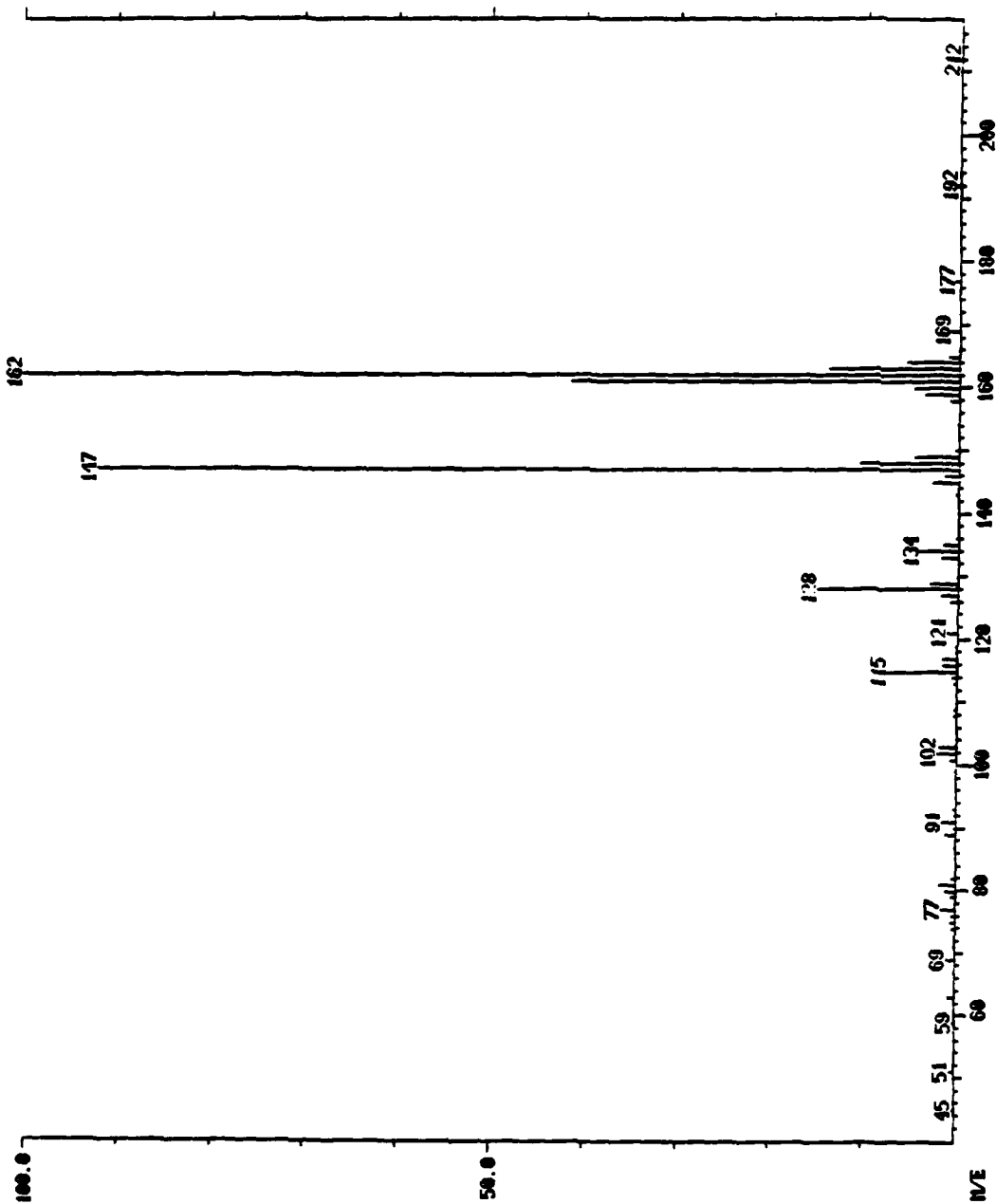


Figure B-3. Mass Spectrum of C₂-Benzothiophene, Figure A-1, Scan No. 2083

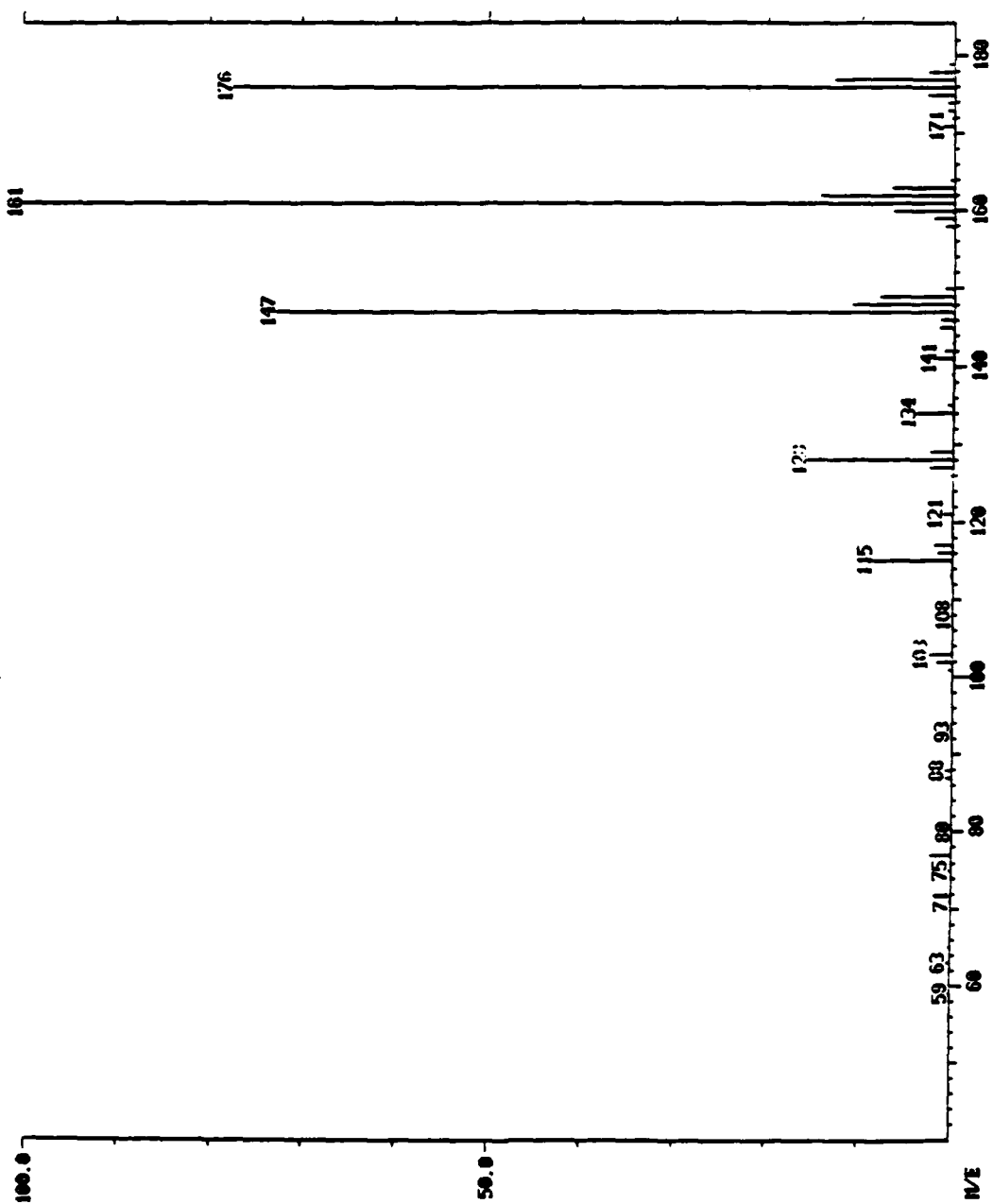


Figure B-4. Mass Spectrum of C₃-Dihydrobenzothiophene, Figure B-1, Scan No. 2194

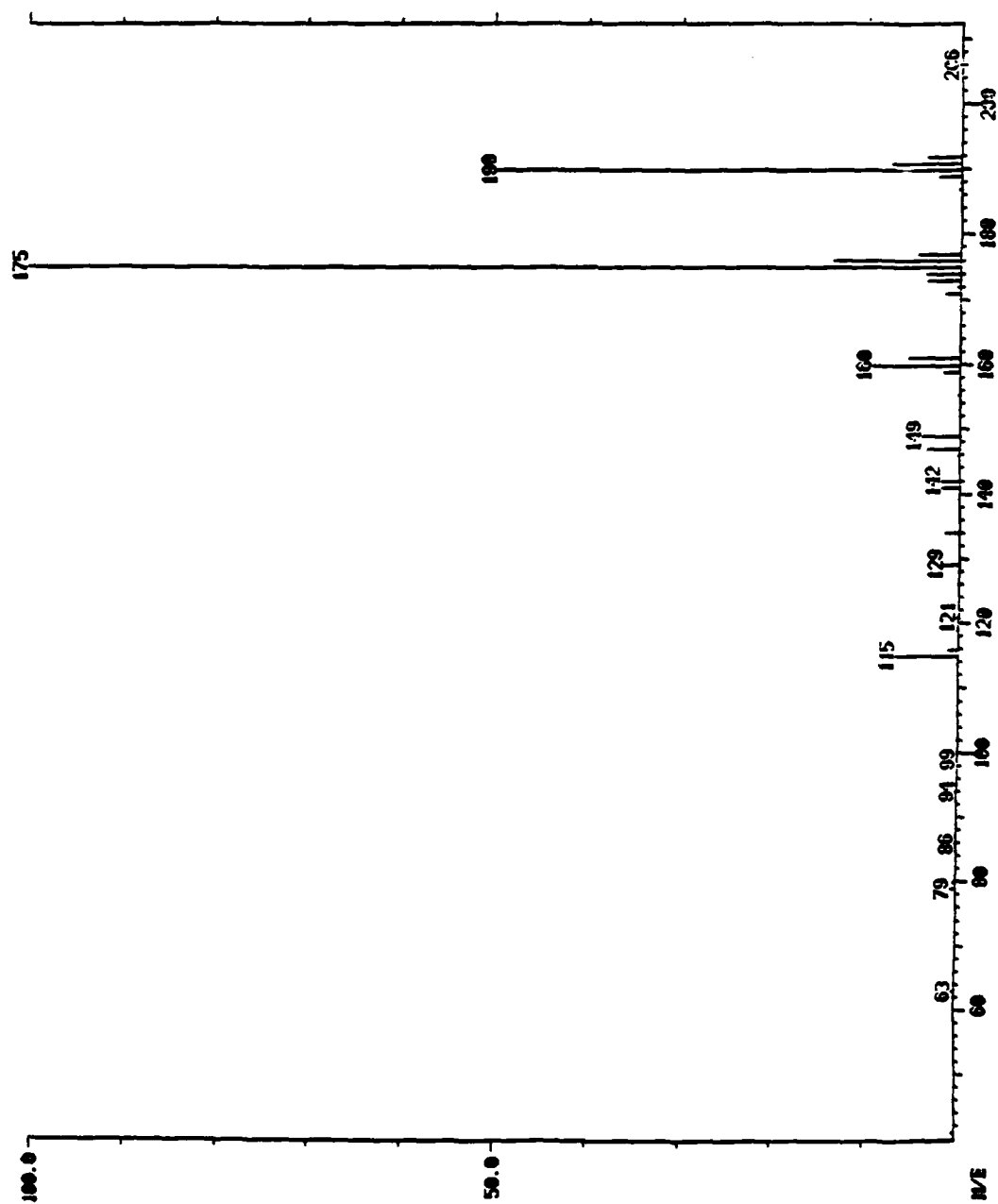


Figure B-5. Mass Spectrum of C_4 -Benzothiophene, Figure B-1, Scan No. 2377

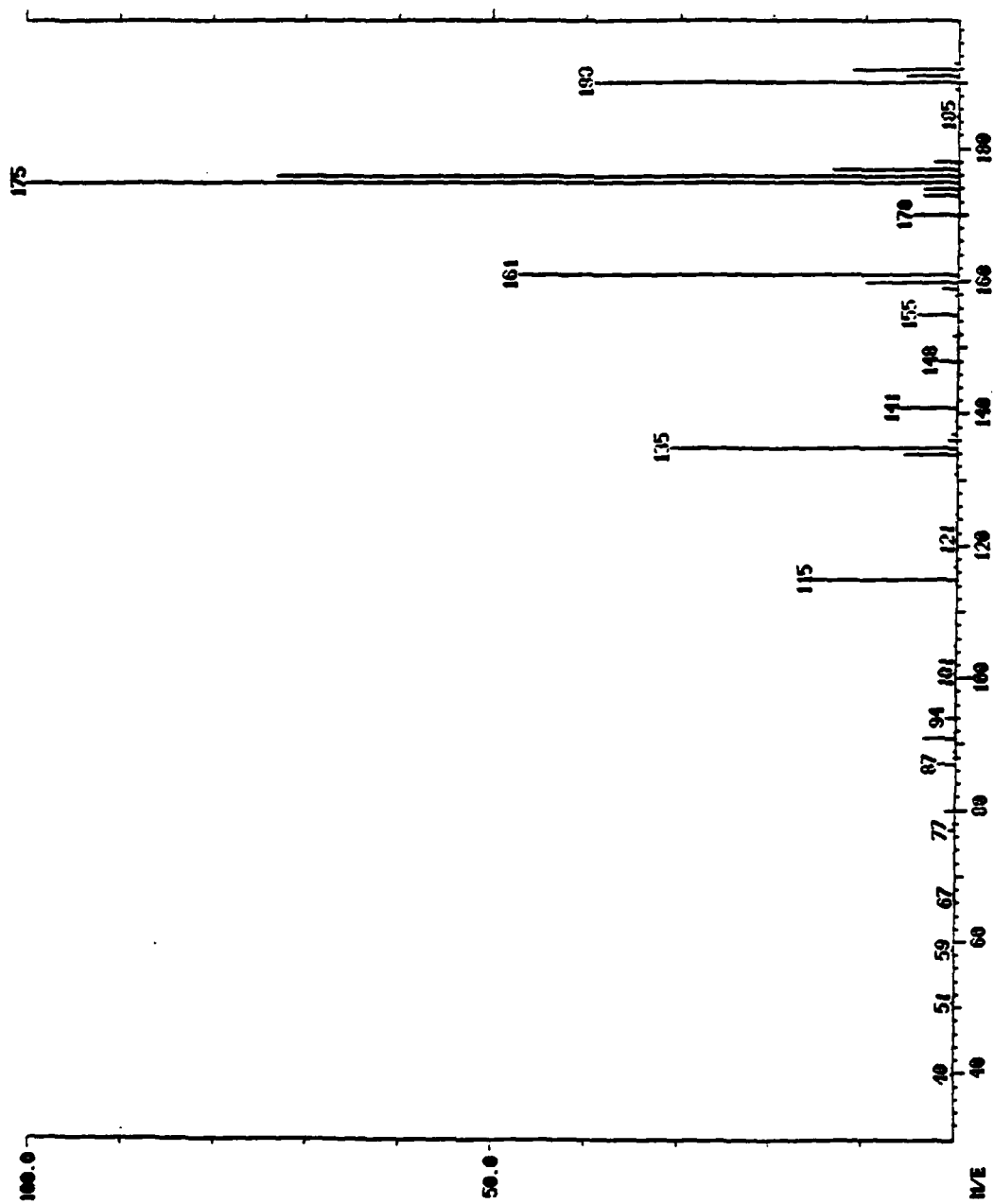


Figure B-6. Mass Spectrum of C₄-Benzothiophene, Figure B-1, Scan No. 2385

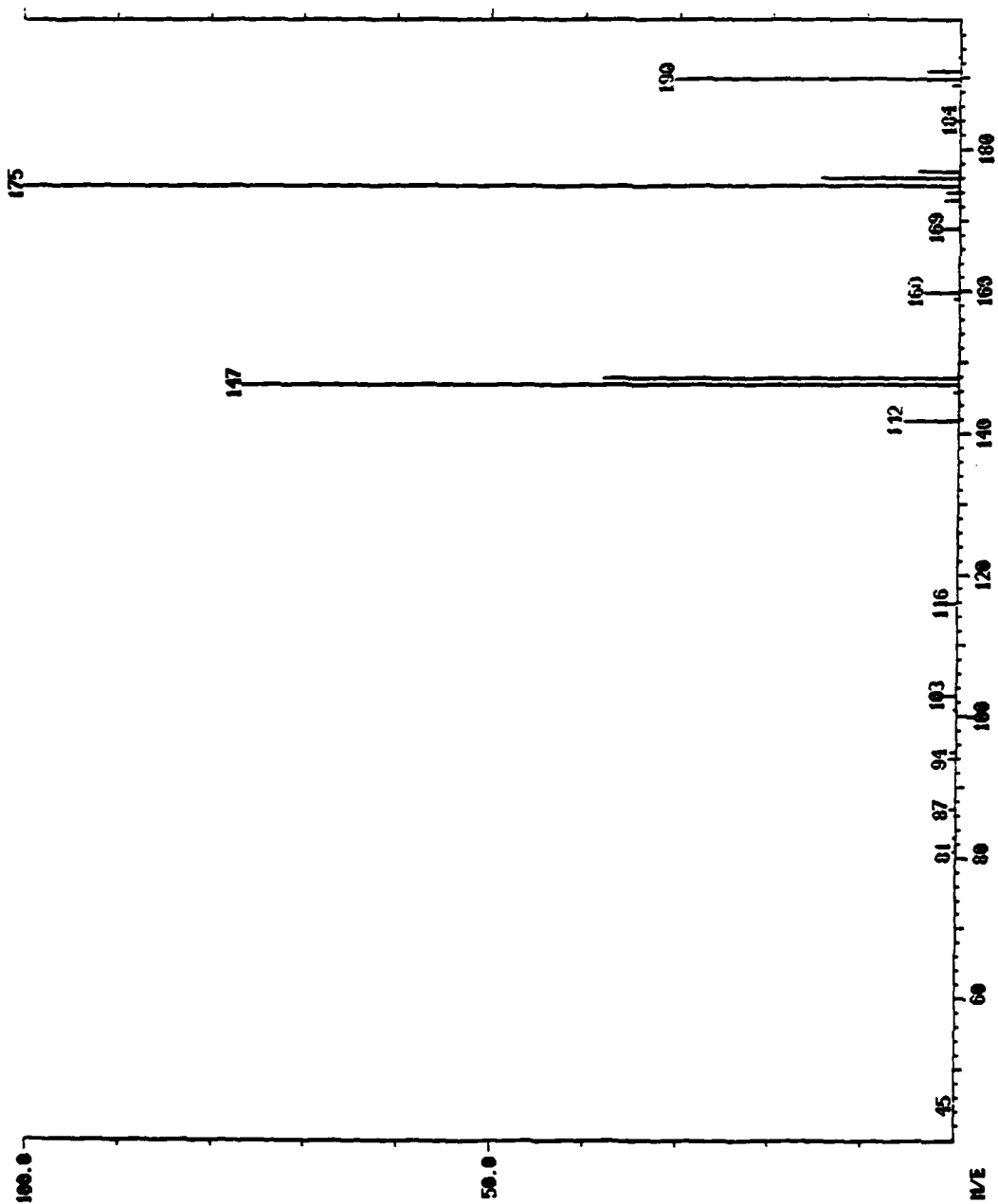


Figure B-7. Mass Spectrum of C_4 -Benzothiophene, Figure B-1, Scan No. 2398

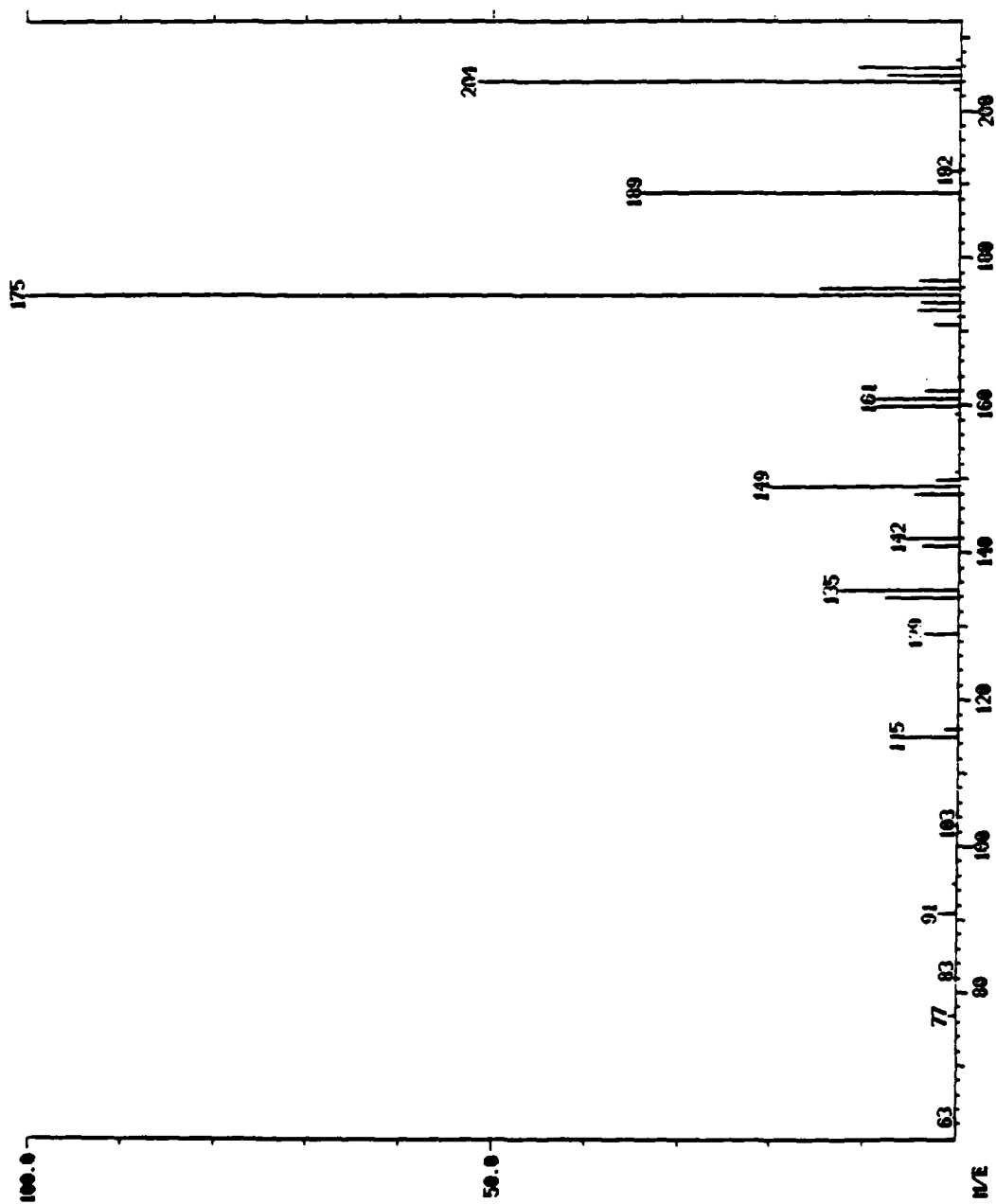


Figure B-8. Mass Spectrum of C₅-Benzothiophene, Figure B-1, Scan No. 2522

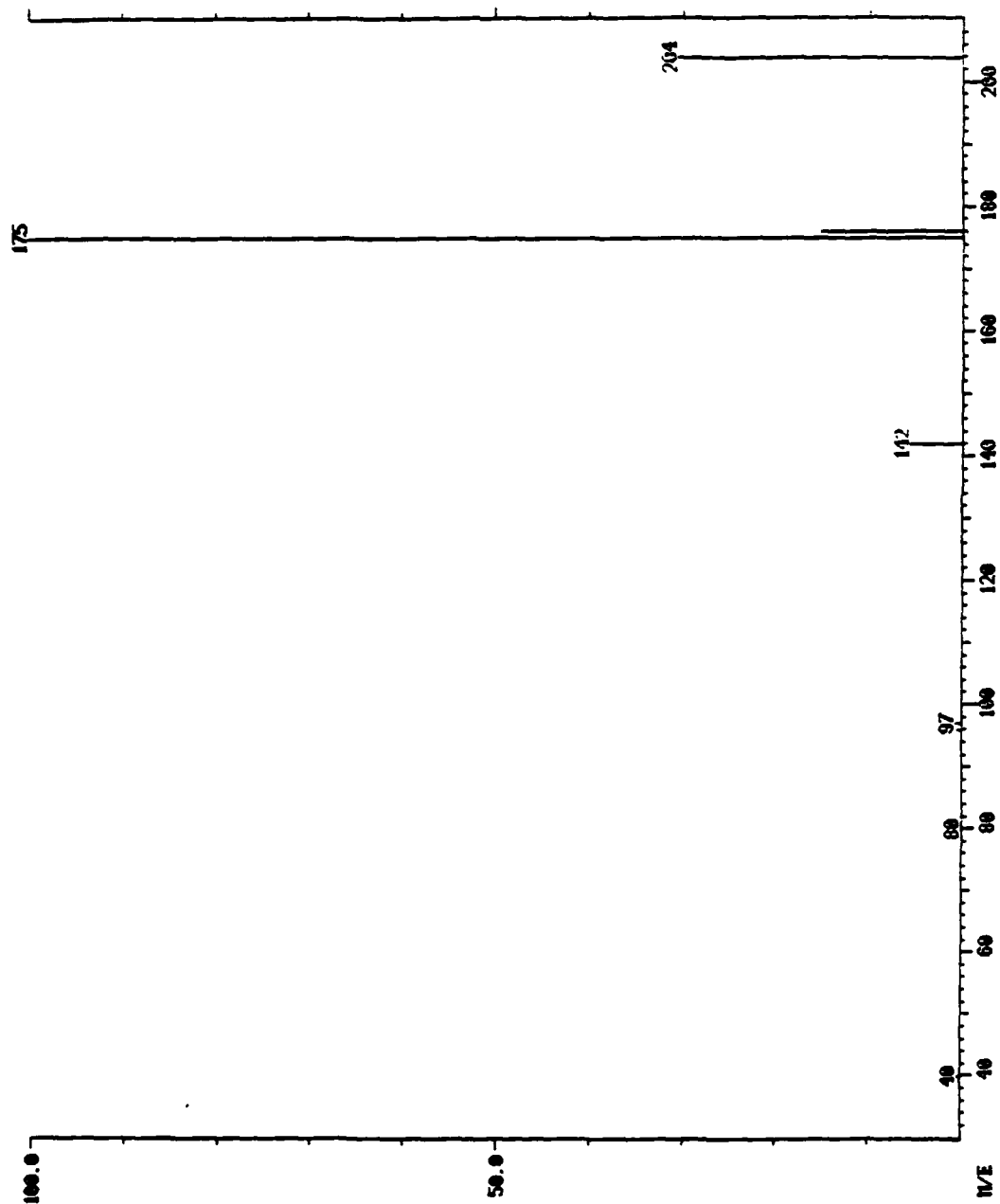


Figure B-9. Mass Spectrum of C₅-Benzothiophene, Figure B-1, Scan No. 2570

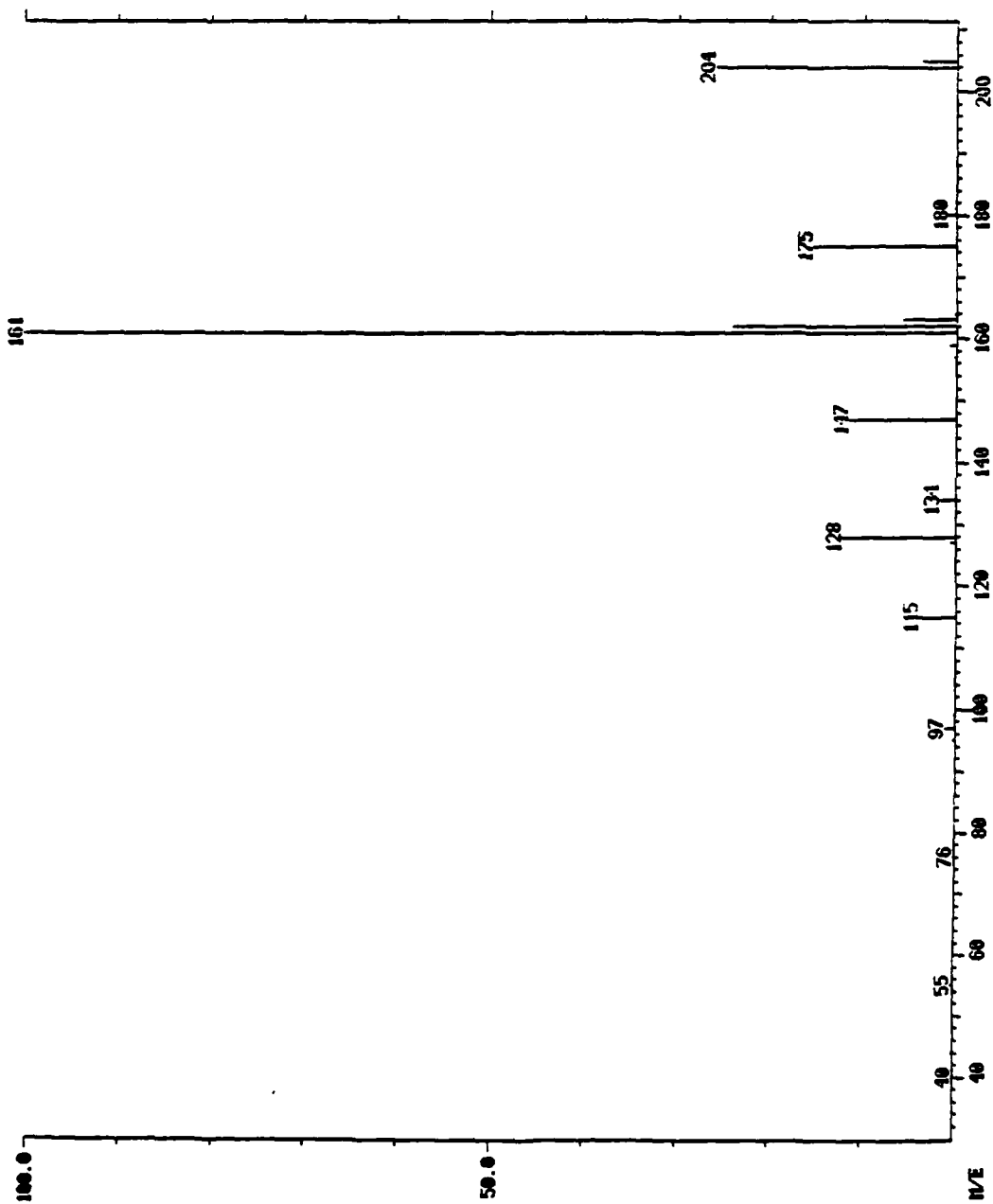


Figure B-10. Mass Spectrum of C₅-Benzothiophene, Figure B-1, Scan No. 2596

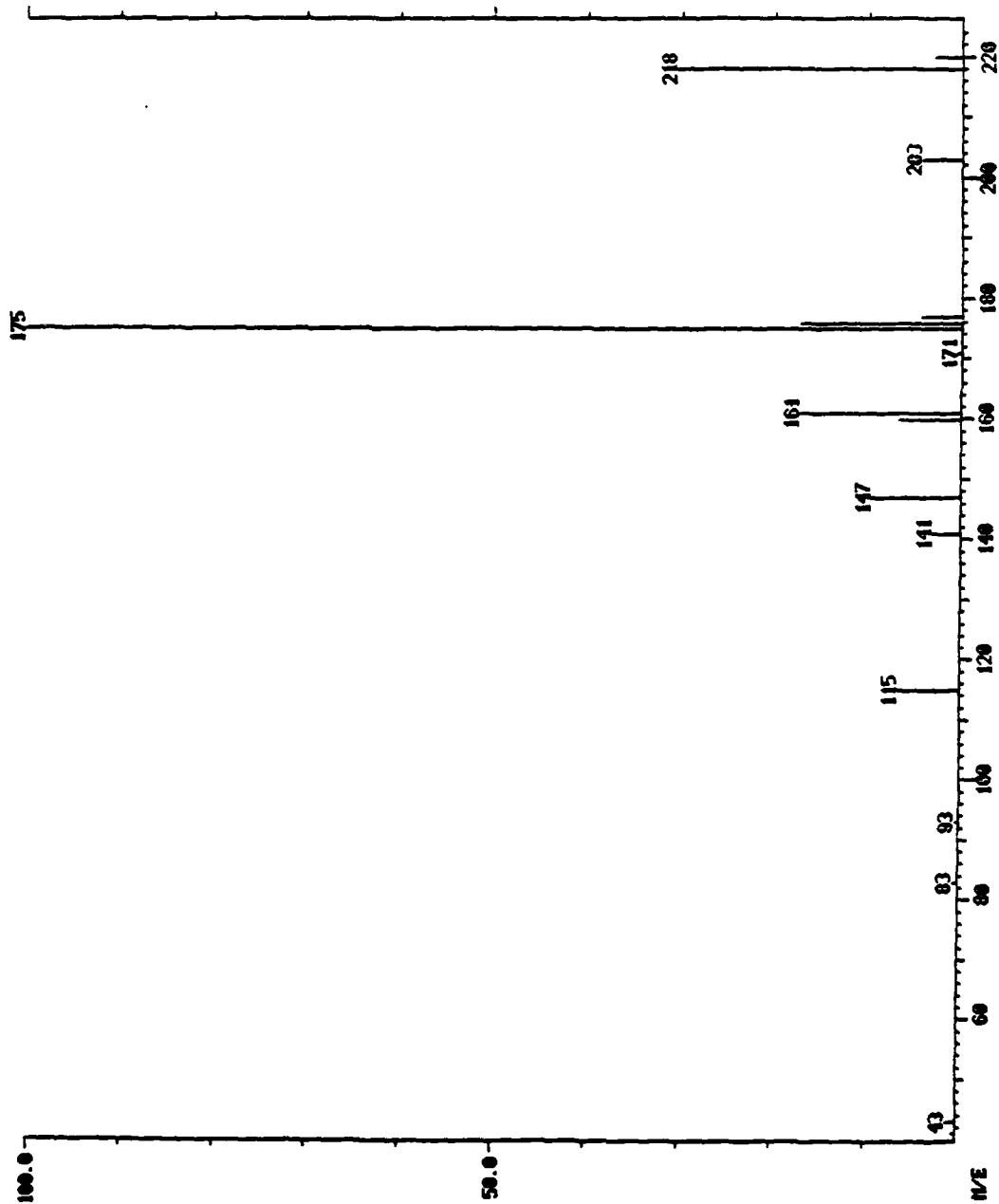


Figure B-11. Mass Spectrum of C_6 -Benzothiophene, Figure B-1, Scan No. 2649

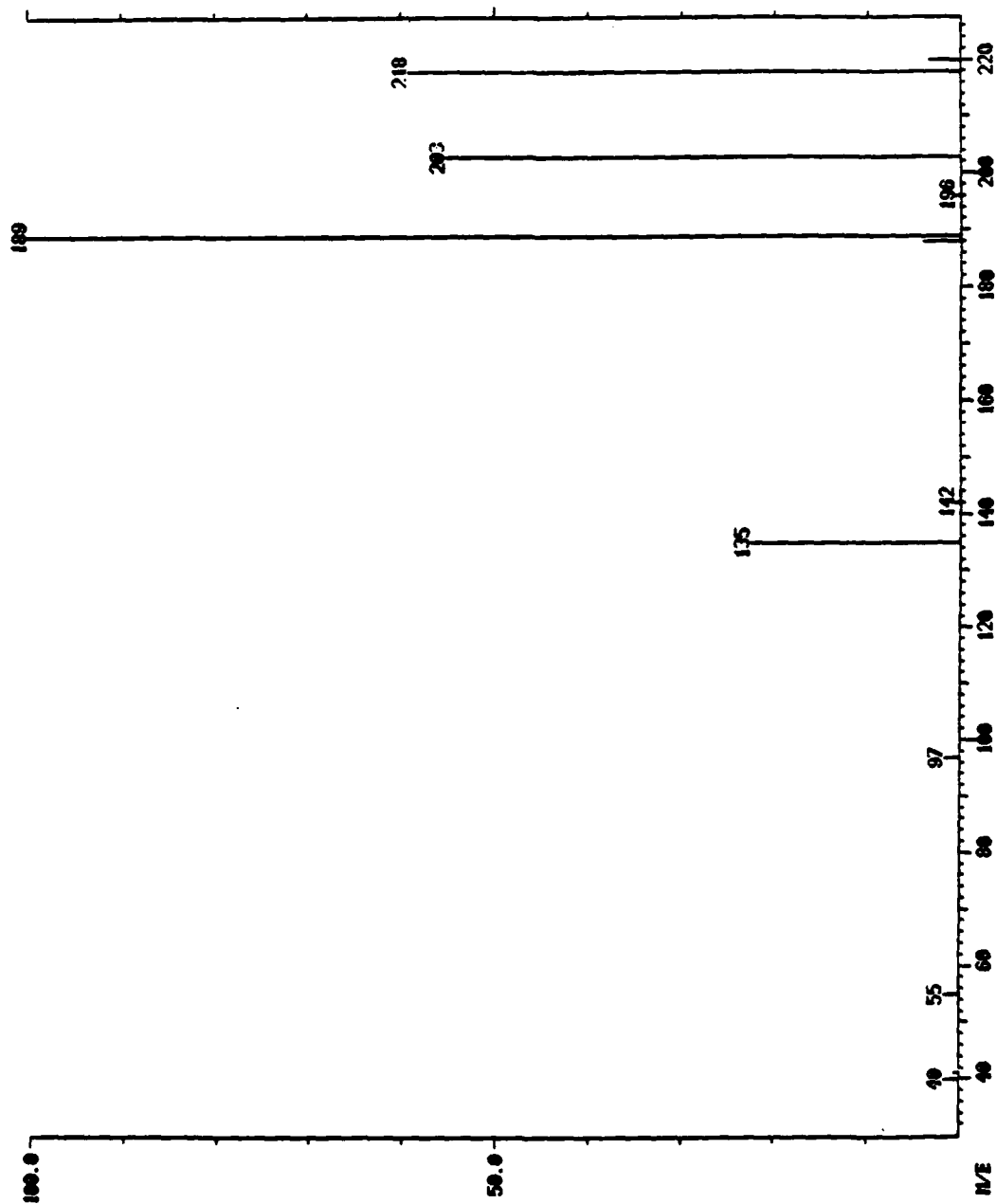


Figure B-12. Mass Spectrum of C_6 -Benzothiophene, Figure B-1, Scan No. 2683

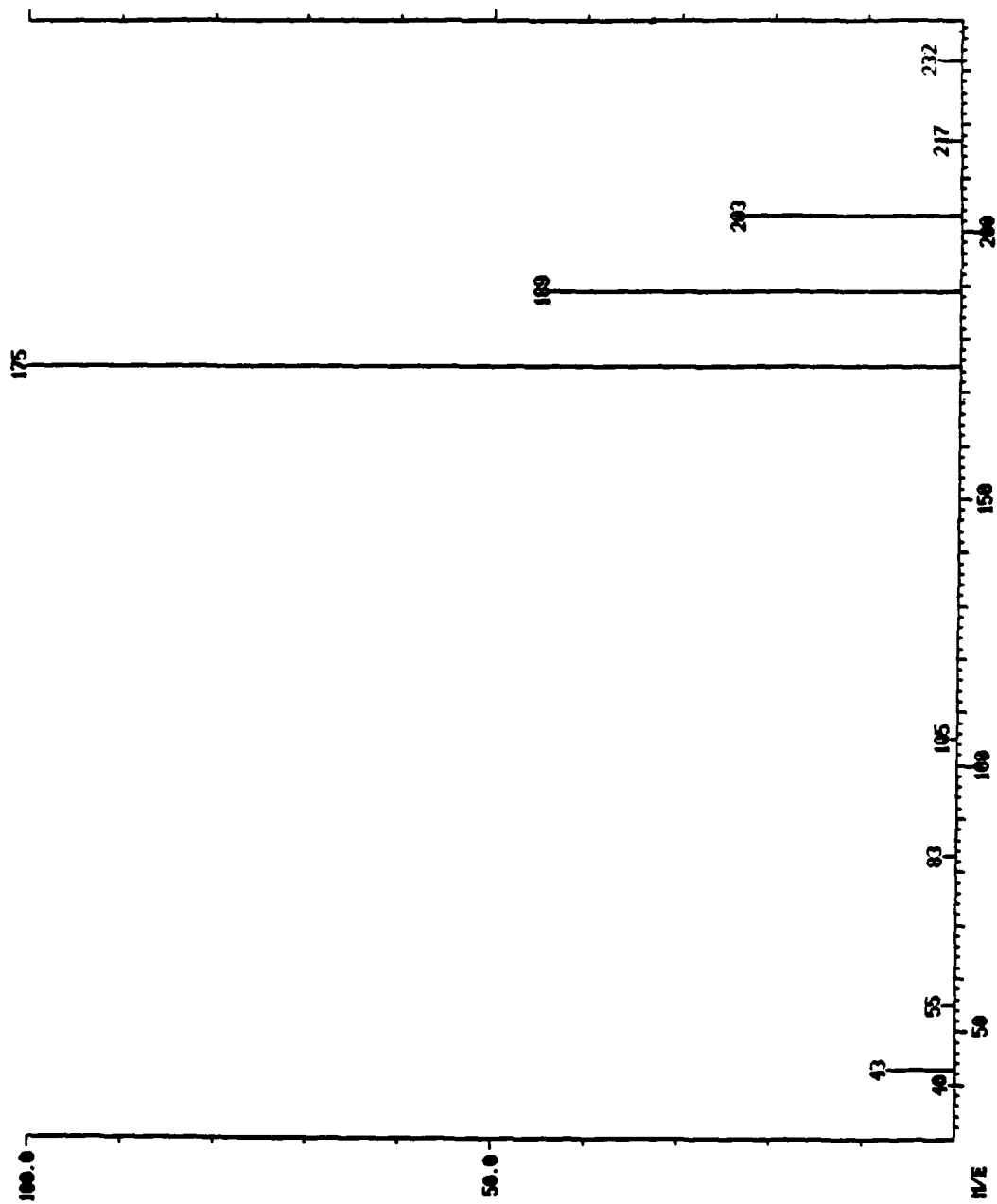


Figure B-13. Mass Spectrum of C₇-Benzothiophene, Figure B-1, Scan No. 2751

APPENDIX C - SAMPLE CALCULATIONS OF PERCENT CARBON UNSATURATION

Masterbatch A

- Krynac 38.50 contains 38% acrylonitrile and therefore 62% butadiene
- In Masterbatch A: 100 g of the total (200 g) formulation is Krynac 38.50
- Butadiene (56 g/mole) contains two carbons (24 g) which are unsaturated
- According to Polysar, Inc., about 60% of the total butadiene content in Krynac 38.50 is in the 1,4- form; the remaining 40% of the butadiene is in the 1,2- form.

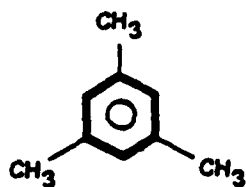
Therefore:

$$\begin{aligned}
 (\% \text{ C} = \text{C}) &= (0.62 \text{ g butadiene/g Krynac})(100 \text{ g Krynac}/200 \text{ g Masterbatch A}) \times \\
 &\quad (24 \text{ g unsaturated carbon}/56 \text{ g butadiene}) \times \\
 &\quad (60 \text{ g 1,4-butadiene}/67 \text{ g total butadiene}) \\
 &= 0.123 \text{ g unsaturated carbon / g Masterbatch A}
 \end{aligned}$$

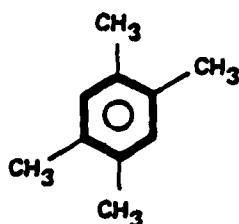
Compound 14310-69-2 = 95A + 5 B

$$\begin{aligned}
 (\% \text{ C} = \text{C}) &= (119.5 \text{ g Masterbatch A} / 125 \text{ g total -69-2}) \times \\
 &\quad (0.123 \text{ g carbon/g Masterbatch A}) \\
 &= 0.118 \text{ g unsaturated carbon/ g -69-2}
 \end{aligned}$$

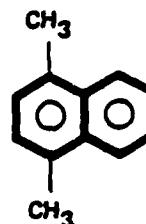
Appendix D. Structures of Chemicals Used in Aromatic and Peroxide Precursor Studies



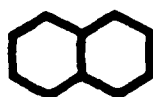
MESITYLENE



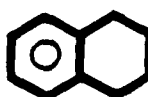
DURENE



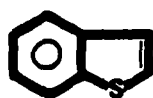
DIMETHYLNAPHTHALENE



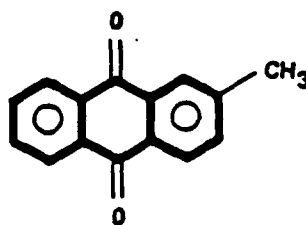
DECALIN



TETRALIN



THIANAPHTHENE



2-METHYLANTHRAQUINONE

APPENDIX E

Estimate of Fraction of Metal Disc Coverage by Additive at 2.0 ppm

This calculation is an attempt to relate the coverage of the disc in the Lucas Tester to the concentration of additive observed at the break point in friction factor measurement. The break point usually occurs at about 2 ppm.

In operation, the disc is constantly replenished with surface liquid from a dropping pipette. Our estimates must be rather crude in this calculation; only a careful adsorption isotherm study can determine the concentration of additive needed to achieve monolayer coverage, which can then be compared with the Lucas Tester break point.

We make the assumption that the disc, area 16 cm^2 , is in contact with sample to a depth of 2 mm. Thus the volume of liquid extracted is 3.2 cm^3 . The density of isooctane is 0.69 gm/cm^3 , therefore the wt. of additive present at 2 ppm is

$$W = (2 \times 10^{-6}) (0.69 \text{ gm/cm}^3) (3.2 \text{ cm}^3) = 4.4 \times 10^{-6} \text{ gm}$$

The additive is mainly di-linoleic acid, MW-560 gm/mole. Thus the additive on the disc consists of

$$\frac{4.4 \times 10^{-6} \text{ gm}}{560 \text{ gm/mole}} = 1.9 \times 10^{-9} \text{ moles or}$$

4.7×10^{15} molecules. If this number of molecules covers the 16 cm^2 disc surface, then the area per molecule is

$$\frac{16 \text{ cm}^2}{4.7 \times 10^{15} \text{ molecules}} = 3.4 \times 10^{-15} \text{ cm}^2$$

In molecular units, this is 34 \AA^2 . The area per molecule of di-linoleic acid, determined by Langmuir surface balance is 20 \AA^2 . The value calculated here of 34 \AA^2 is perhaps fortuitously close, but the conclusion drawn is only this: the break point occurring at 2 ppm is not inconsistent with the notion that lubricity enhancement by additive reaches a limiting value when the metal surface achieves monolayer coverage.

It should be noted here that the coverage is at least by weak chemisorption as the metal disc does show memory effects and can return to reading high friction factors for harsh fuels only after a thorough detergent cleaning.